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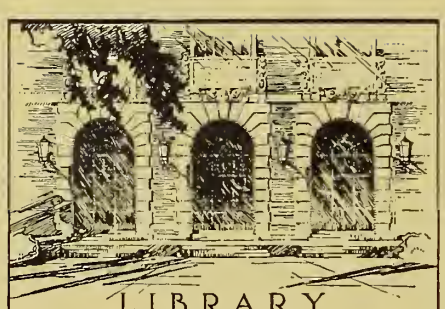

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CIVIL ENGINEERING STUDIES
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REMOVAL OF PHOSPHATES IN SECONDARY SEWAGE TREATMENT EFFLUENT BY SAND FILTRATION

By
CHU-CHUAN HSU

Supported by
DIVISION OF WATER SUPPLY AND POLLUTION CONTROL
U. S. PUBLIC HEALTH SERVICE
RESEARCH PROJECT WP-18

DEPARTMENT OF CIVIL ENGINEERING
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
MAY, 1964

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ABSTRACT

This research was undertaken in order to investigate the effect of sand filtration on phosphates in secondary sewage treatment effluent. The study intends to discover if sand filtration could be developed as a practical tertiary treatment for phosphate removal following the conventional secondary treatment process, so that the stream pollution problem resulting from over enrichment of phosphates can be controlled. Six columns have been set up for the study. The phosphate removal efficiency of each column under several operating conditions was examined during a nineteen-week period. The results reveal that a minor but significant amount of phosphates in all forms has been removed by the columns under study. Greater phosphate removal was observed in the early dates, the effect decreasing with time. The effectiveness of removal was inversely proportional to the hydraulic feed loading per dose. The best result was obtained by dosing the sand column 12 times a day at a dose rate of 10.3 to 11.6 lbs P_2O_5/acre/dose. Coarse gravel was less effective in removing phosphates than sand. Adsorption and assimilation are two major mechanisms in phosphate removal by columns. The adsorptive capacity decreased with time. Considerable phosphate removal after two months operation was mainly due to the biological assimilation when the adsorption effect approached its limit. It was found that the phosphate removal efficiency of the column after elution with tap water can be restored to its initial high removal capacity. Therefore, it is concluded that an effective tertiary treatment in removing phosphates from the secondary treatment effluent by sand filtration can only be accomplished if the unit is intermittently fed and periodically elutriated.

TABLE OF CONTENTS

		Page
ACKNOWLEDGMENTS		iii
ABSTRACT		iv
LIST OF TABLES		vii
LIST OF FIGURES		viii
CHAPTER 1:	INTRODUCTION	1
	1.1. Sanitary Engineering Significance	1
	1.2. Phosphates in Sewage	2
	1.3. Phosphates in Surface Waters	3
	1.4. Purpose of Study	5
CHAPTER 2:	CHEMISTRY OF PHOSPHATES	6
	2.1. Occurrence	6
	2.2. Valence States of Phosphorus	6
	2.3. Three Forms of Phosphorous Acid	7
	2.4. Phosphorus Compounds	7
	2.5. Phosphate Metabolic Reactions	11
	2.6. Mechanisms of Phosphate Removal in Sand Column	13
CHAPTER 3:	PROCEDURE OF STUDY	15
	3.1. Preparation of Columns	15
	3.2. Operation of Columns	17
	3.3. Analytical Method	21
	3.4. Principle of Phosphate Determination	22
CHAPTER 4:	EXPERIMENTAL RESULTS	25
	4.1. Phosphate Removal in Sand Columns	25
	4.2. Phosphate Removal versus Time	42
	4.3. Phosphate Removal versus Feeding Rate	42

TABLE OF CONTENTS (continued)

		Page
4.4.	Phosphates Removed by Adsorption and Assimilation	49
4.5.	Operating Condition of Columns	57
4.6.	Elution of Columns	59
4.7.	Investigation of Column Medium at the End of Experiment	63
CHAPTER 5:	DISCUSSION OF THE RESULTS	66
5.1.	Phosphates Removed by Sand Columns	66
5.2.	Phosphate Removal Efficiency Decreased with Time	68
5.3.	Relationship between Feeding Rate and Phosphate Removal	69
5.4.	Effects of Physical Adsorption and Biological Assimilation	70
5.5.	Significance of Column Elution	71
CHAPTER 6:	CONCLUSIONS	74
REFERENCES		76
APPENDICES		79
Appendix A.	Procedures for the Determination of Ortho-, Condensed-, and Total-Phosphates	79
Appendix B.	Calibration Curve for the Determination of Phosphate Concentration	81
Appendix C.	Data of Phosphate Concentration in Column Influents and Effluents	82

LIST OF TABLES

Table		Page
1	The Mechanisms of Phosphate Transfer in Waterway System	4
2	Column Packing Data	17
3	Loading Rates and Feeding Rates for the Columns	19
4	Average and Standard Deviation Data of Phosphate Removal by Sand Columns	45
5	Percent COD Removal by Sand Columns	58
6	Cumulative Removal of Total Phosphates in Nineteen Weeks	58
7	Total Phosphates Removed and Amount that can be Eluted	61
8	Phosphate Removal Before and After Elution	61
9	Elution Data of Column 5	62
10	Variation of Moisture, Volatile Solids and Bacteria Counts of Columns with Depth of Sand	64
11	Orthophosphate Concentration in Column Influents and Effluents (First Period)	82
12	Orthophosphate Concentration in Column Influents and Effluents (Second Period)	83
13	Condensed Phosphate Concentration in Column Influents and Effluents (First Period)	84
14	Condensed Phosphate Concentration in Column Influents and Effluents (Second Period)	85
15	Organic Phosphate Concentration in Column Influents and Effluents (First Period)	86
16	Organic Phosphate Concentration in Column Influents and Effluents (Second Period)	87
17	Total Phosphate Concentration in Column Influents and Effluents (First Period)	88
18	Total Phosphate Concentration in Column Influents and Effluents (Second Period)	89
19	Percentage Removal of Total Phosphates (First Period)	90
20	Percentage Removal of Total Phosphates (Second Period)	91

LIST OF FIGURES

Figure		Page
1	Schematic Diagram of Sand Column	16
2	Line Diagram of Sand Column	20
3	Comparison of Orthophosphate Removal between First and Second Period	26
4	Orthophosphate Concentration in Column 1 (First Period)	27
5	Orthophosphate Concentration in Column 2 (First Period)	28
6	Orthophosphate Concentration in Column 3 (First Period)	29
7	Orthophosphate Concentration in Column 4 (First Period)	30
8	Orthophosphate Concentration in Column 5 (First Period)	31
9	Orthophosphate Concentration in Column 6 (First Period)	32
10	Orthophosphate Concentration in Column 1 (Second Period)	33
11	Orthophosphate Concentration in Column 2 (Second Period)	34
12	Orthophosphate Concentration in Column 3 (Second Period)	35
13	Orthophosphate Concentration in Column 4 (Second Period)	36
14	Orthophosphate Concentration in Column 5 (Second Period)	37
15	Orthophosphate Concentration in Column 6 (Second Period)	38
16	Percent Removal of Condensed Phosphates in First Period	40
17	Percent Removal of Condensed Phosphates in Second Period	40
18	Percent Removal of Organic Phosphates in First Period	41
19	Percent Removal of Organic Phosphates in Second Period	41
20	Average Concentration of Total Phosphates in Column Influents and Effluents	43
21	Comparison of Total Phosphate Removal between First and Second Period	44
22	Average Concentration of Total Phosphates Removed by the Columns	46
23	Total Phosphate Removal versus Time (I)	47

LIST OF FIGURES (continued)

Figure		Page
24	Total Phosphate Removal versus Time (II)	48
25	Phosphate Removal versus Dose Rate	50
26	Cumulative Total Phosphate Removal by Column 1	51
27	Cumulative Total Phosphate Removal by Column 2	52
28	Cumulative Total Phosphate Removal by Column 3	53
29	Cumulative Total Phosphate Removal by Column 4	54
30	Cumulative Total Phosphate Removal by Column 5	55
31	Cumulative Total Phosphate Removal by Column 6	56
32	Elution of Columns with Tap Water	60
33	Evaluation of Moisture, Volatile Solids, and Bacterial Density in Sand Columns	65
34	Elution Curve of Column 5	73

CHAPTER 1: INTRODUCTION

1.1. Sanitary Engineering Significance

Excessive enrichment of receiving waters by nutrient-rich wastes is becoming a major water pollution problem in many areas. It has been recognized that ordinary domestic sewage is a rich source of the nutrients required by phytoplankton and the degree of eutrophication is dependent largely upon the supply of phosphates (1)(2)(3)(4)(5). The effluents of sewage treatment plants usually contribute fertilizer in the form of nitrates and phosphates to a receiving water. The nutrient properties of all phosphates promote prolific aquatic growths. The well-recognized ills resulting from such growths are (a) algal toxicity, (b) aesthetic harm, such as a soupy appearance, taste and odors in potable water, and odors in the environs from algal decomposition and (c) buildup of a biochemical oxygen demand (6)(7)(8)(9)(10).

Since the household detergent package is composed of about 30 percent of phosphates as builders and the use of detergents is still in increase (11)(12), the phosphate concentration in domestic sewage has been increased continuously. A substantial portion of phosphates tends to pass through conventional treatment plants into receiving waters. Their fertilizing properties give rise to prolific growth of both heterotrophic and autotrophic organisms in lakes and streams. Obnoxious tastes and odors in waters may result. Such effects may interfere with the natural uses of the lakes and may influence the shoreline land use (13)(14)(15). It has also been reported that the condensed phosphates may interfere with normal coagulation and sedimentation operation in water treatment processes in case of receiving waters used for water supply (16)(17)(18)(19). A study on the occurrence and degradation of condensed phosphates in Illinois rivers by Engelbrecht and

Morgan revealed that the condensed phosphates used in detergents would, at relatively high concentrations, interfere with coagulation and settling. They also showed that the concentration of condensed phosphates in Illinois surface supplies generally less than 0.5 mg/l; this concentration did exert a very slight interference that could be overcome readily by either a moderate increase in coagulation dosage or an increase in settling time (20)(21). Therefore, the removal of phosphates in common sewage treatment effluent to an acceptable degree before discharging into receiving water bodies has become a matter of concern in recent years.

1.2. Phosphates in Sewage

Domestic sewage is relatively rich in phosphorus compounds. Most of the inorganic phosphorus was contributed by human wastes as a result of the metabolic breakdown of proteins and elimination of the liberated phosphates in the urine. The amount of phosphorus released is a function of protein intake (22). However, the rapidly increasing use of synthetic detergents has led to the presence of greater amounts of phosphorus compounds in sewage than ever. Prior to the development of synthetic detergents, the content of inorganic phosphorus usually ranged from 2 to 3 mg/l and organic forms varied from 0.5 to 1 mg/l. It has been estimated that domestic sewage probably contains from two to three times as much inorganic phosphorus at present as it did before synthetic detergents became widely used (23).

Phosphates occur in sewage in the forms of orthophosphate, condensed phosphate, and organic phosphate, which are present in both soluble and insoluble forms. The orthophosphates may be derived from dishwashing compounds, hydrolytic products of polyphosphates, and fertilizers. The condensed phosphates occur as sodium tripolyphosphate and tetrasodium pyrophosphate which

are builders in synthetic detergents. Organic phosphates are the result of body wastes and biological growths (16).

The condensed phosphates revert to orthophosphates hydrolytically at a very fast rate. Orthophosphate can be transformed to organic phosphates by metabolic conversion.

1.3. Phosphates in Surface Waters

The phosphates present in surface waters may come from sewage effluents discharged from treatment plants or may come from the drainage of agricultural fertilizer carried over by runoff (24). The quantity of phosphate contributed to surface waters in Illinois by domestic sewage was estimated on the basis of stream analysis to range from 7.1×10^{-3} to 87.3×10^{-3} pounds per capita per day (25). A survey on Illinois rivers indicates that almost half of the total phosphate present comes from the drainage of agricultural land (20)(26). It was also confirmed that the complex phosphates degrade to the simple orthophosphate in the presence of stream biota, the rates of degradation varying according to the physical, chemical, and biological conditions encountered (27).

The transfer of phosphate in a waterway system is caused by mass transfer of phosphate between the surface water and the hypolimnium or by chemical change from complex type of phosphate to simple one. The changes that occur in phosphate form may be brought about by one or more mechanisms as shown in Table 1 (28).

Table 1

THE MECHANISMS OF PHOSPHATE TRANSFER IN WATERWAY SYSTEM

Type of Mechanism	Description
Physical	a. Settling of insoluble phosphates.
	b. Redispersion of previously settled matter due to turbulence.
Chemical	a. Precipitation.
	b. Hydrolysis of condensed phosphates.
Physico-Chemical	a. Adsorption on suspended matter in surface water followed by settling.
	b. Peptizing effect of condensed phosphates in promoting dispersion of previously settled matter.
Biochemical	a. Conversion of organic phosphates to inorganic compounds which may or may not be soluble. Inorganic phosphate products may be formed in either hypolimnium or in surface water.
	b. Synthesis of autotrophic organisms, particularly algae, which utilize dissolved inorganic phosphates as nutrients.

1.4. Purpose of Study

It is the purpose of this experiment to observe the effect on phosphates in secondary sewage treatment effluent as they pass through aerated sand filtration columns.

As previously described, domestic sewage is an important source of phosphorus which is an essential food element of aquatic organisms. The nutrient properties of all phosphates may promote prolific aquatic growths as the result of discharging sewage into streams. Such effect gives rise to severe stream pollution problems in many areas. Sawyer (13), from his experience, concluded that phosphorus concentration in excess of 0.01 ppm could be expected to produce algal blooms of such density as to cause nuisance. Ordinary domestic sewage contains from 2 to 4 ppm of phosphorus resulting from the use of household detergents. It can be predicted that the content of phosphates in domestic sewage will increase proportionally with increasing use of synthetic detergent. Unfortunately, the conventional sewage treatment processes cannot effectively reduce the phosphate concentration to such an extent that no stream pollution problems result. It seems that a tertiary treatment of sewage is valuable as far as the phosphate effect is concerned. However, this study intends to discover if the sand filtration could remove significant amount of phosphates in the usual sewage treatment plant effluent. Thus a tertiary treatment might be practically established following conventional secondary treatment process, and the stream pollution problems that are attributed to phosphates might be controlled.

CHAPTER 2: CHEMISTRY OF PHOSPHATES

2.1. Occurrence

Phosphorus does not occur free in nature. It is found in form of phosphates in the minerals chlorapatite, fluorapatite, vivianite, wavelite, and phosphate rock. It occurs in small quantities in granite rocks and in all fertile soil. Phosphorus is an essential constituent of protoplasm, nervous tissue, and bones (29). Of the nearly two hundred different phosphate minerals, only one, fluorapatite, is commercially important. This mineral, $Ca_5F(PO_4)_3$, is mined from large secondary deposits originating from the bones of dead creatures deposited on the bottom of prehistoric seas and from bird droppings in ancient rookeries. In the United States, the major phosphate deposits are in Florida, Tennessee, and the Montana-Idaho region (30).

Phosphorus is necessary to life. A certain amount of phosphorus is always contained in every cell of every living plant and animal. It exists in the cell nucleus which is the structural element most intimately associated with the phenomena of growth and reproduction.

2.2. Valence States of Phosphorus

The chemistry of phosphorus is somewhat complex because of the several valence states that phosphorus can assume and the fact that changes in valence can be brought about by living organisms.

The lowest valence state of phosphorus, -3, is represented by phosphine (PH_3); and the phosphonium salts such as PH_4I. Both phosphine and the phosphonium salts are active reducing agents.

Phosphites which have a +3 valence number of phosphorus are formed by the action of active reducing agents on the phosphates. Further reduction may convert them into still lower valence states. They are readily reoxidized

to phosphates, hence serve as active reducing agents.

The most important valence state of phosphorus is +5. This is represented by the pentoxide, three different phosphoric acids (meta-, pyro-, and ortho-phosphoric acid), and numerous phosphate salts (31)(32).

2.3. Three Forms of Phosphorous Acid

Phosphorus pentoxide, P_2O_5, is remarkable for its vigorous union with water to form phosphoric acids. The direct union of phosphorus pentoxide with water yields chiefly metaphosphoric acid ($H_2P_2O_6$). The acid combines with more water to form pyro-phosphoric acid, $H_4P_2O_7$, and the orthophosphoric acid, H_3PO_4 (32). The reactions are shown as follows:

$$P_4O_{10} + 2H_2O \rightarrow 2H_2P_2O_6$$

Metaphosphoric acid

$$H_2P_2O_6 + H_2O \rightarrow H_4P_2O_7$$

Pyrophosphoric acid

$$2H_4P_2O_7 \rightleftarrows H_2P_2O_6 + 2H_3PO_4$$

Orthophosphoric acid

2.4. Phosphorus Compounds

Both inorganic compounds of phosphorus and organically bound phosphorus are of significance in sanitary engineering practice. In this study, three kinds of phosphate have been taken into consideration; i.e., orthophosphate, condensed phosphate (or polyphosphate) and organic phosphate.

2.4.1. Orthophosphates

Orthophosphates are derived from orthophosphoric acid, H_3PO_4. The acid contains three hydrogens which can be replaced stepwise by reaction with a base to form various salts. The orthophosphates commonly encountered in sanitary engineering practice are listed as follows (30).

NaH_2PO_4	Monosodium phosphate (Primary sodium phosphate)
Ha_2HPO_4	Disodium phosphate (Secondary sodium phosphate)
Na_3PO_4	Trisodium phosphate (Tertiary sodium phosphate)
$(NH_4)_2HPO_4$	Diammonium phosphate

2.4.2. Condensed Phosphates

The salts of polyphosphoric acids consisting of two or more phosphorus are usually called complex phosphates or polyphosphates. The major source of condensed phosphates in domestic sewage is attributed to commercial detergents widely used today. The synthetic detergents contain a relatively high proportion (more than 30%) of inorganic condensed phosphate salts such as sodium tripolyphosphate, tetrasodium pyrophosphate, and sodium hexametaphosphate (16)(33)(34).

$Na_5P_3O_{10}$	Sodium tripolyphosphate (STP)
$Na_4P_2O_7$	Tetra sodium pyrophosphate (TSPP)
$Na_3(PO_3)_6$	Sodium hexametaphosphate

The phosphate builders can assist detergency by enhancing surface-active properties and by acting as suspending, dispersing, and sequestering

agents. Sodium hexametaphosphate can soften water through sequestering action, and is also an efficient dispersing agent. Sodium tripolyphosphate increases the foaming and dispersing tendencies of detergents and, in addition, possesses sequestering power. Tetrasodium pyrophosphate is another phosphate builder that exhibits dispersing and sequestering properties (35).

The condensed phosphates have a tendency to react with water to undergo hydrolysis or reversion to orthophosphates. This property has been observed by various investigators (36)(37)(38)(39). These investigators have found that some of the environmental factors affecting the rate of reversion are enzymes, gels of inorganic oxides (hydrated oxides of iron and aluminum), complexing agents (calcium, magnesium or sodium), pH, temperature and concentration of phosphates. It has been reported that when the ratio of cellular material to phosphate is high and when conditions for metabolizing phosphate are favorable, the hydrolysis of condensed phosphates is accelerated by a factor of 10^5 to 10^6 due to enzymatic activity (16). Thus it can be expected that condensed phosphates will be hydrolized at a much faster rate in an activated sludge plant than in the water way. The rate of reversion to the orthophosphate increases rapidly as the temperature approaches the boiling point. The rate is also increased by lowering the pH (23).

2.4.3. Organic Phosphates

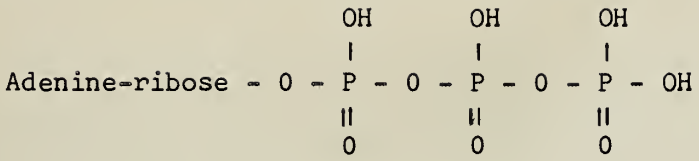
The organisms all require phosphorus for reproduction and synthesis of new cell tissue. The limitation in amounts of this element is sometimes the factor that controls their rate of growth. Organic phosphates in living tissues may be in the form of phospholipides and nucleotides. Phospholipides are not only the principal structural compounds of living matter but also the main constituents of the food. All kinds of nucleotides consist of a

phosphate residue. The most important nucleotides are adenine nucleotides because they have a particular function as carriers of phosphate residues. The autotrophic organisms, such as algae, utilize inorganic phosphates to produce organic end products -- protoplasm. Therefore, the organic phosphates are the results of biological growth. Meanwhile, all the biochemical reactions are enzyme reactions in which the enzymes serve to initiate the reactions and also to control the speed. Several important materials in biological metabolisms called coenzymes are complex phosphate compounds. They must be present for certain enzymes to act. The most important coenzymes are DPN (diphosphopyridine nucleotide), ATP (adenosine triphosphate) and CoA (coenzyme A) (40). DPN serves as a hydrogen carrier in a number of reactions catalyzed by dehydrogenases. The best-known function of ATP is in the oxidation of glucose. Coenzyme A is a derivative of pantothenic acid; it functions in fatty-acid metabolism and synthesis.

The three principal classes of organic phosphate derivatives of biological importance are (1) phosphate esters, (2) mixed anhydrides of phosphoric acid and organic acids or enols, and (3) phosphamides. Organic phosphate esters are split into the corresponding alcohol and phosphate when a suitable enzyme is added to their aqueous solutions. In the absence of phosphatase (enzyme), the phosphate esters are quite stable and do not undergo spontaneous hydrolysis.

The most important of high-energy phosphate bonds is that of ATP. Its formula shows that ATP consists of one molecule of adenosine monophosphate and two molecules of phosphate which are linked to each other and to adenosine monophosphate by pyrophosphate bonds. The bond between the terminal phosphate residue of ATP and the adjacent phosphate residue is unstable and is easily hydrolyzed in presence of the enzyme adenosine triphosphatase. The structure

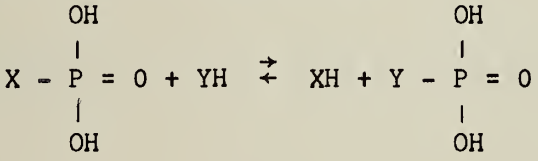
of ATP is shown below:



2.5. Phosphate Metabolic Reactions

The combination of organic molecules with phosphate is one of the most important metabolic reactions because many of the organic substances can be metabolized in the phosphorylated state only. In fact, fermentation and many other metabolic reactions do not take place unless phosphate is present (41).

The formation of organic phosphate compounds, their cleavage, and the transfer of phosphate residues from one organic compound to another can be represented generally by following equation.



where X = PO_3H_2 is a phosphate donor and YH a phosphate acceptor.

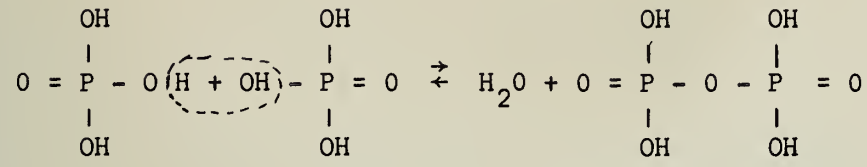
If X is a hydroxyl group and Y is an organic residue, the equation represents phosphorylation of the compound YH.

If X is an organic residue and Y is a hydroxyl group, then YH is water, and the equation stands for the hydrolytic cleavage of the organic phosphate compound.

If both X and Y are organic residues, the equation represents transfer of phosphate from X to Y.

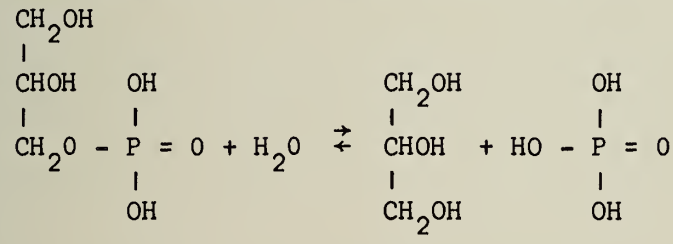
The derivatives of pyrophosphoric acid formed in metabolic reactions can be described as the example of the first case. The pyrophosphoric acid

is formed by the loss of one water molecule from two molecules of phosphoric acid.



or 2 Phosphoric acid $\rightleftarrows$ H_2O + Pyrophosphoric acid

The hydrolytic cleavage of an organic phosphate ester, such as glycero phosphate, is shown by the reaction below:



or Glycerophosphate + H_2O $\rightleftarrows$ Glycerol + Phosphate

The above reaction is the illustration of the second case.

As previously mentioned, adenosine triphosphate (ATP) is the most important phosphate donor of living matter. In the presence of the enzyme, ATP is hydrolyzed to ADP and inorganic phosphate.

ATP + H_2O $\rightarrow$ ADP + Phosphate

In the phosphorylation of glucose, the phosphate residue of ATP transfers to glucose.

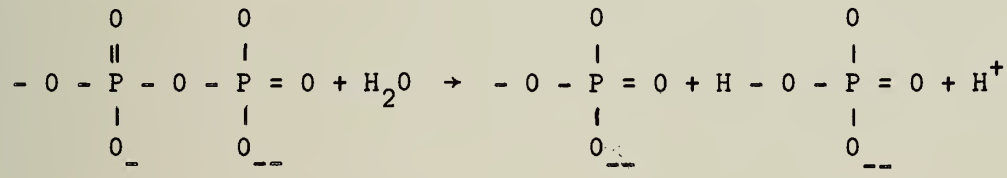
ATP + Glucose $\rightarrow$ ADP + Glucose-6-phosphate

Actually, this reaction is obtained by the summation of the following reactions:

$$ATP + H_2O \rightarrow ADP + Phosphate$$

$$Glucose + Phosphate \rightarrow Glucose\text{-}6\text{-}phosphate + H_2O$$

Generally, every reaction in metabolism and photosynthesis involved the hydrolysis of this tripolyphosphate to its pyrophosphate. The hydrolysis of chain phosphates occurs through splitting of a P-O-P linkage as indicated in the following chemical equation (30):



In neutral solution at room temperature, the rate for this process is extremely slow. However, enzymes increase the rate many thousandfold. The equilibrium between ATP, water, ADP and the orthophosphate ion is strongly shifted toward the hydrolysis product, adenosine diphosphate and the orthophosphate ion. Because of these facts, organic reactions in biological systems are naturally controlled so that life can exist.

2.6. Mechanisms of Phosphate Removal in Sand Column

The mechanisms of phosphate removal in sand column may include physical, chemical, and biological effects. The phosphorus that exists in bacterial cells as an essential constituent will be readily released in the form of orthophosphate upon decomposition. Condensed phosphates have been known to have a tendency to convert to the ortho form hydrolytically. As

mentioned early, the hydrolysis of condensed phosphates is greatly accelerated by enzymatic activity when conditions for metabolism of phosphate are favorable. Orthophosphates can be removed by either physical adsorption or biological assimilation. Adsorption takes place on the surface of medium (sand or gravel) and of bacteria slime. The theory and function of adsorption have been well illustrated in many early studies (42)(43)(44)(45). The orthophosphates are also reduced by incorporation into biological mass. The organisms grown on media surface utilize dissolved inorganic phosphates as nutrients. Therefore, by the metabolism of bacteria, the orthophosphates will be reverted to organic phosphates. Then, it is obvious that by the mechanisms stated above, the high concentration of phosphate in secondary sewage treatment effluent, when applied to pass through the sand column, must be reduced to some extent.

CHAPTER 3: PROCEDURE OF STUDY

3.1. Preparation of Columns

It was decided to make six columns for the study so that six different operating conditions resulting from either varying the feed loadings or changing the dosing frequency could be examined at the same time.

3.1.1. Construction

The columns were constructed of four-inch diameter Plexiglass pipe and packed with three feet of sand according to the sketch shown in Figure 1. The columns had their tops widely open and their bottoms closed. Each column had two holes near the bottom. One was always opened as the exit of effluent. Another served as an air inlet and was often closed except when applying compressed air to aerate the column once for awhile. The air inlet allowed the compressed air coming in and passing through the sand layers thus maintained the sand column in an aerobic condition.

3.1.2. Packing

The columns were set up on a steel frame. The granular medium previously sieved to reject very fine materials was weighed and wet-packed into the column to get the fine stickings out. The packing was done in stages with back wash of tap water and air to get a clean sand. The sand depth was adjusted to about 3 feet and with about the same quantity of sand in each column. The saturated permeability and porosity of the sand column are indicated in Table 2. The permeability of each column was determined by passing a fixed quantity of water at constant head through the column and noting the time elapsed. The pore volume of the sand column was obtained approximately by saturating the dry column with tap water until there was a

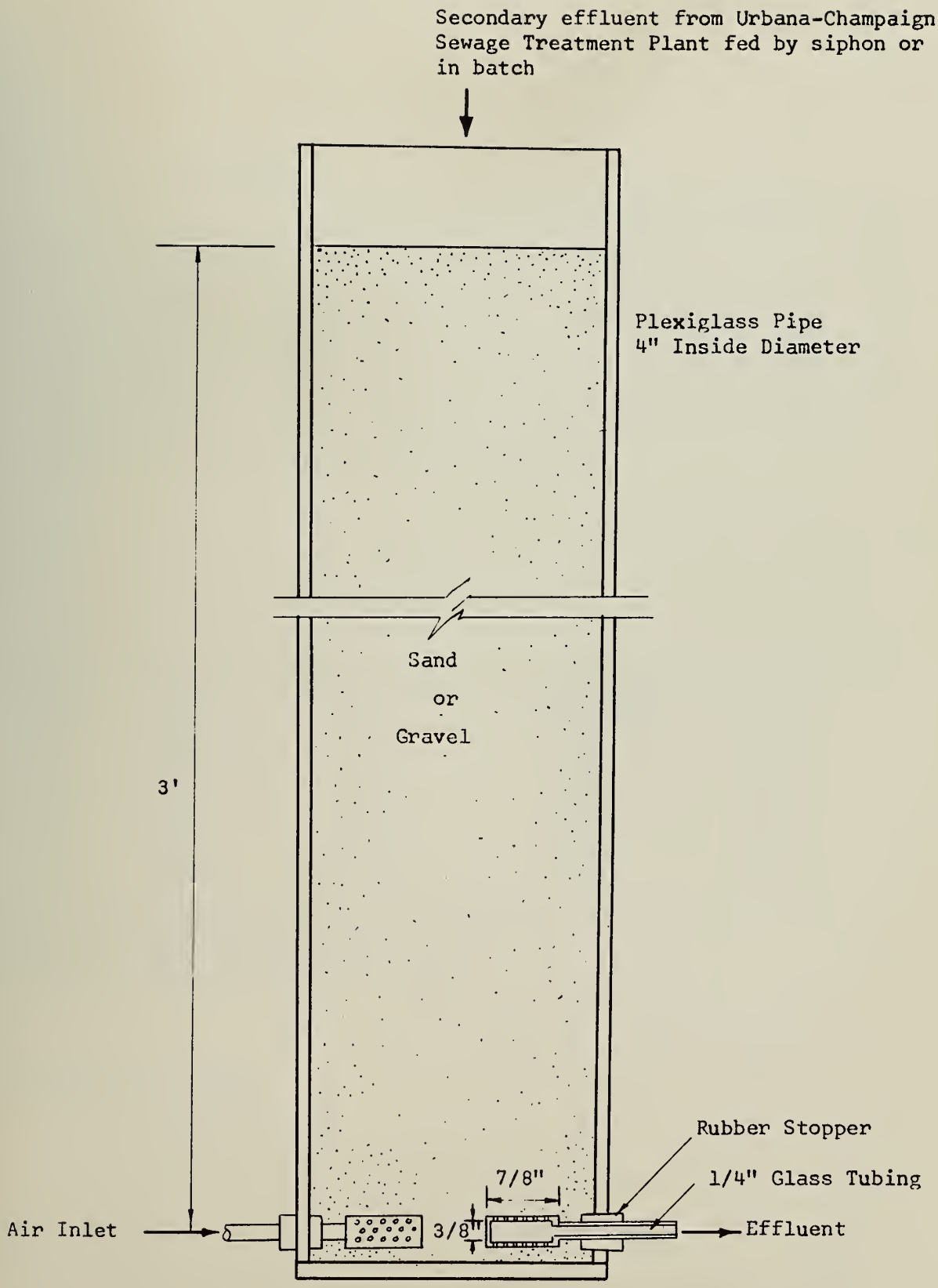


Figure 1. Schematic Diagram of Sand Column

trace of water over the sand surface. The volume of tap water used was a rough value of the pore volume.

3.1.3. Media Used

Among the six columns, five of them were packed with Muscatine fine sand, whereas the sixth column was packed with pea gravel of 3/8" to 1/4" size. Muscatine sand is usually used for rapid gravity filter in water supply. A sieve analysis was performed on the sand to obtain the uniformity coefficient and the effective size of sand. The sand was found to have a uniformity coefficient of 1.3 and an effective size of 0.29 mm.

Table 2

COLUMN PACKING DATA

Column No.	Medium Type	Medium Weight gms.	Permeability gal/ft/day	Porosity
1	Sand	12,150	2,380	0.425
2	Sand	12,150	2,570	0.467
3	Sand	12,120	2,370	0.441
4	Sand	12,150	3,370	0.498
5	Sand	12,150	2,540	0.511
6	Gravel	13,750	6,300	0.421

Uniformity Coefficient of Sands was 1.3.
Effective size of Sands was 0.29 mm.
Gravel size ranged from 1/4" to 3/8".

3.2. Operation of Columns

3.2.1. Feed Solutions

To study the removal of phosphates from secondary treatment effluent by means of aerated sand filters, the treated sewage from activated sludge effluent was taken from Urbana-Champaign Sanitary District Sewage Treatment Plant as the influent to the columns. The total phosphate concentration of

feed solution was found to range from 23.0 to 63.0 mg/ℓ and to have an average of 45.93 mg/ℓ as P_2O_5. A synthetic feed solution consisting of Bactopeptone, monosodium phosphate and packaged detergent was applied to one of the columns after it had been operated on sewage for two months. The exact concentration of phosphate in the synthetic solution was determined each time when its effluent was taken for the evaluation of phosphate removal.

3.2.2. Feeding Rates

The feeding rate of each column was different; Columns 1, 2, and 3 had the same amount fed per day but the frequency of dosing was different, Columns 4, 5, and 6 had the same feeding sequence but different amounts fed per day. Therefore, six different feed conditions were involved in this column study. After they had been operated for two months, the feeding rates were altered. The feeding schedules have been listed in Table 3.

3.2.3. Performance

The columns were fed daily according to the schedules described in Table 3. It was decided to run intermittent doses to the sand columns because it is the purpose to obtain quantitative information on phosphate removal by these sand filtration columns. Moreover, the operation of intermittent feed provided better aeration conditions at most of the resting period.

A feed bottle containing a certain amount of feed solution was provided for each column. A syphon system was set up for intermittent dosing as shown in Figure 2, where syphon A and B were used to control the dosing rate as well as the feed sequence. A screw clamp attached to syphon A was provided to control the discharge rate of the feed solution from the feed bottle to the dose cylinder. The clamp was so adjusted that the feed volume

Table 3

LOADING RATES AND FEEDING RATES FOR THE COLUMNS

Column No.	Total Flow l/day		Feed Sequence Times/day		Feed Rate m/day		Dose Rate 10^3 gal/acre		Phosphate Loading lbs P_2O_5/acre/dose		Phosphate Loading gms P_2O_5/m^2/day	
	A	B	A	B	A	B	A	B	A	B	A	B
1	2.5	12.5	1	1	0.30	1.50	340.0	1700.0	123.5	696.0	13.1	78.0
2	2.5	2.5*	4	4	0.30	0.30	85.0	85.0	30.9	29.1	13.1	14.7
3	2.5	2.5	12	12	0.30	0.30	28.4	28.4	10.3	11.6	13.1	14.7
4	4.0	4.0	4	4	0.48	0.48	131.0	131.0	47.6	53.7	21.9	23.5
5	6.0	12.0	4	4	0.73	1.46	203.6	407.2	73.8	166.5	31.9	71.6
6	10.0	10.0	4	12	1.09	1.09	302.2	100.7	109.9	41.2	47.2	53.5

A = First period
B = Second period
*Synthetic feed solution

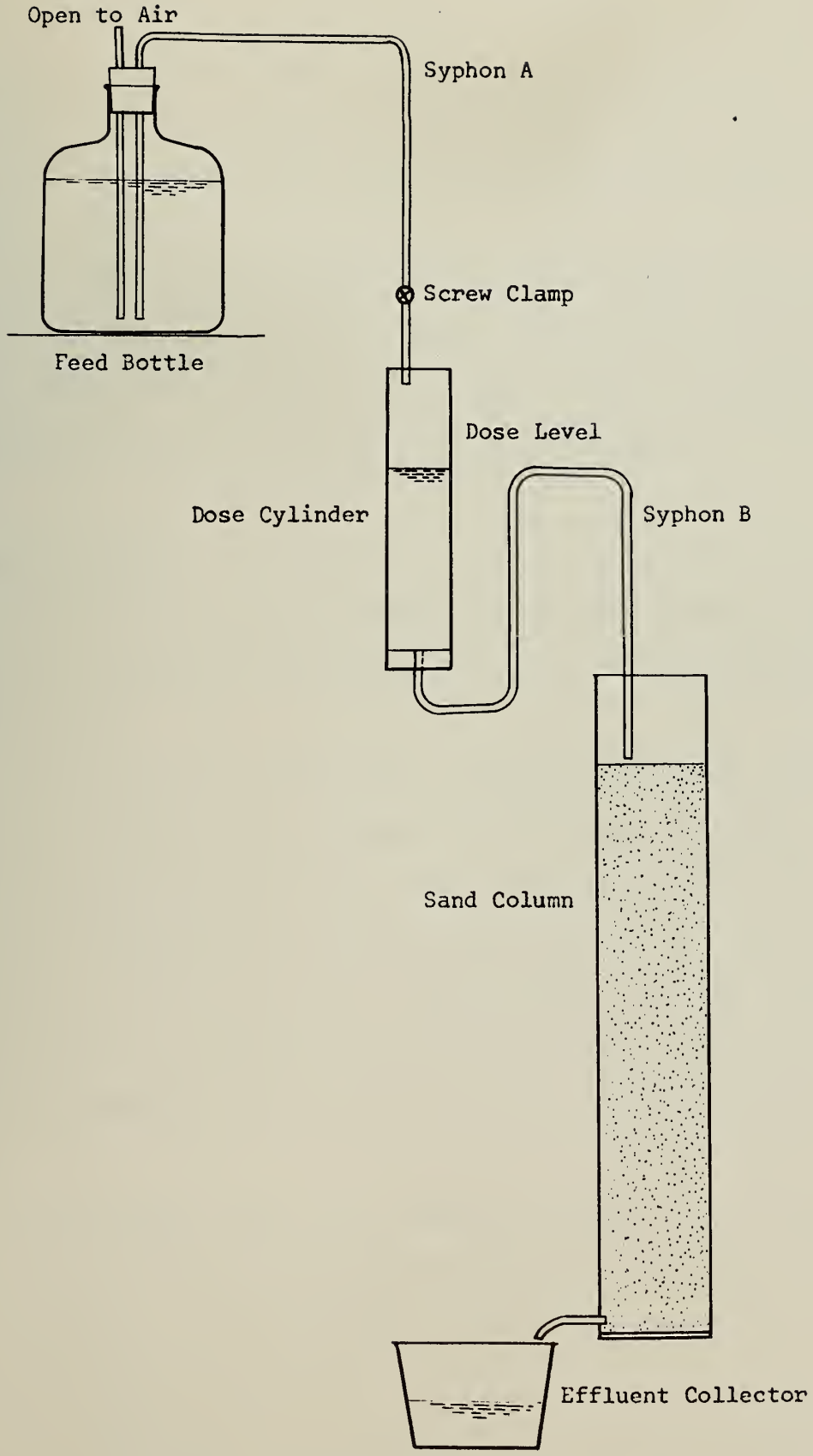


Figure 2. Line Diagram of Sand Column

per dose was collected in the dose cylinder in the required interval between feedings, say 2.5 liters in 2 hours. Syphon B was set at the same level as the water level in the dose cylinder. When the feed solution in dose cylinder gradually raised to the dose level, syphon B drained the feed solution to the sand column very rapidly.

The effluents of the columns were collected by the buckets separately. Samples of influents and effluents from six columns were taken for chemical analysis to determine the phosphate concentration of each. The effect of phosphate removal was then calculated from the data analyzed.

3.3. Analytical Method

Samples were analyzed by the extraction and hydrolysis procedure proposed by the committee of Association of American Soap and Glycerine Producers (AASGP) (46).

Orthophosphate was determined by running a colorimetric extraction directly on the original sample. Condensed phosphate was obtained by boiling the samples in aqueous sulfuric acid to convert to orthophosphate, running the colorimetric determination, and subtracting the previously determined orthophosphate value from the result. Total phosphate including inorganic and organic phosphate was determined by wet-ashing method and the quantity of organic phosphate was obtained by subtracting total inorganic phosphate from this value.

The colorimetric method used ammonium molybdate to form phosphomolybdate which was extracted with benzene-isobutanol, reduced with stannous chloride and read on a Coleman spectrophotometer at wave length 630 mμ with red filter and a light path of 2 cm.

It is experienced that the method has the advantage of reducing hydrolysis during the test and enables turbid samples to be processed without

a filtration step (16). The method is of more sensitivity and of less interference as compared with other methods. It has a high reliability of result even at concentrations below 0.1 mg/ℓ (47).

3.4. Principle of Phosphate Determination

The use of colorimetric method in this study makes the measurement of orthophosphate free from serious interference resulting from the hydrolysis of condensed phosphate. Because the affecting factors such as the pH condition, extraction time, and temperature were so controlled that the conversion of condensed phosphate to orthophosphate was prevented (48)(49).

Both condensed and organic forms of phosphate are converted to orthophosphate for measurement. The chemistry involved in the determination of orthophosphate is essentially as follows:

$$PO_4^{\equiv} + 12(NH_4)_2MoO_4 + 24H^+ \rightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^+ + 12H_2O$$

The above chemical equation shows that under acid condition phosphate ion will combine with ammonium molybdate to produce a complex compound called ammonium phosphomolybdate. This matter forms a yellow precipitate when sufficient amount of phosphate is present. After extraction with benzene-isobutanol mixture, all the yellow compound will be extracted from sample and remains in the solvent mixture. With concentration of phosphate usually found in sanitary analysis, the yellow color so produced is not discernible. In order to make it feasible for colorimetric determination, other means of color development are necessary. In this study, stannous chloride was used as the reducing agent for this purpose, not only because of the fact that stannous chloride solution is more easily prepared and has much longer effective life but also that it increases the sensitivity and gives a better result.

The molybdenum contained in ammonium phosphomolybdate is readily reduced by stannous chloride to produce a blue-colored sol known as molybdenum blue. The extent of this blue color is proportional to the amount of phosphate present. Excess ammonium molybdate is not reduced and, therefore, does not give interference. The reaction involved with stannous chloride as the reducing agent may be represented in a quantitative manner as follows:

$$(NH_4)_3PO_4 \cdot 12MoO_3 + Sn^{--} \rightarrow \text{(molybdenum blue)} + Sn^{4+}$$

The blue color thus derived makes the colorimetric method highly applicable.

Condensed phosphate may be converted to orthophosphate by boiling samples that have been acidified with 8N sulfuric acid for at least 30 minutes. This is because all the condensed phosphates gradually hydrolyze in aqueous solution and revert to ortho form, and the rate of reversion is a function of temperature and pH. The converting rate increases rapidly as the temperature approaches the boiling point, and is also increased by lowering pH. The orthophosphate formed from the condensed phosphate is measured in the presence of orthophosphate originally present in the sample. The amount obtained represents total inorganic phosphate and the condensed phosphate portion is calculated by difference as follows:

Total inorganic phosphate - Orthophosphate = Condensed phosphate

Organic phosphate is obtained by wet-ashing method in which the sample is digested with concentrated sulfuric acid and nitric acid to insure complete decomposition of the organic phosphate to ortho form. The result

represents the total phosphate including inorganic and organic compounds. The amount of organic phosphate is obtained from following formula

Total phosphate - Total inorganic phosphate = Organic phosphate

The detail procedures of phosphate determination have been described in Appendix A. A calibration curve for the determination of phosphate concentration is presented in Appendix B.

CHAPTER 4: EXPERIMENTAL RESULTS

4.1. Phosphate Removal in Sand Columns

The columns started working on July 3, 1963, and lasted about 19 weeks. During this period, samples from every column were taken for phosphate analysis. The determinations included ortho-, condensed-, and organic-phosphate. The data obtained have been presented in Table 11 through Table 16 (see Appendix C).

As described in previous chapter, the feeding rates of columns were changed after the columns were operated for two months, and a synthetic solution was applied to Column 2 during the last two months. Owing to this change in operation, the data for all forms of phosphates were listed in two separated parts representing two periods, before and after changing feed loadings. The first period was from July 3 to September 8, and the second period was from September 9 to November 11. The analytic work was not performed during the period of the first three weeks of September because of the vacation, therefore, the data of this period were not obtained. However, the feed schedule was operated constantly without interruption.

4.1.1. Orthophosphates

The variation of orthophosphates in the influents and the effluents of columns were shown graphically in Figure 4 through Figure 15. The removal of orthophosphates during the first period was found to be more effective and consistent than that during the second period. Figure 3 shows that in the second period, the removal was relatively small as compared to the first period. In many instances, the orthophosphate concentrations in the effluents during the second period were greater than that in the influents. Such situation was also found in the first period, but it will be interesting to note

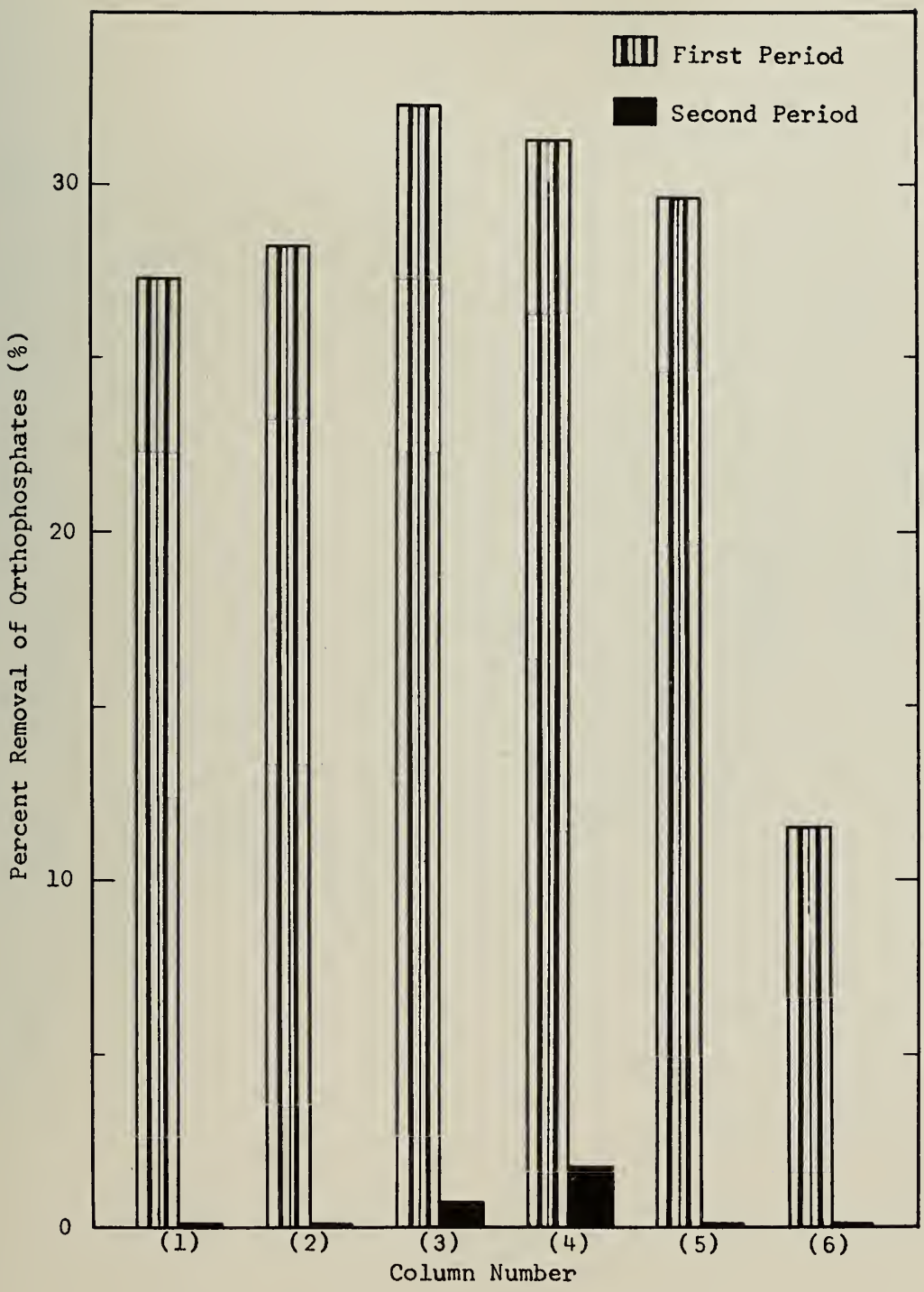


Figure 3. Comparison of Orthophosphate Removal Between First and Second Period

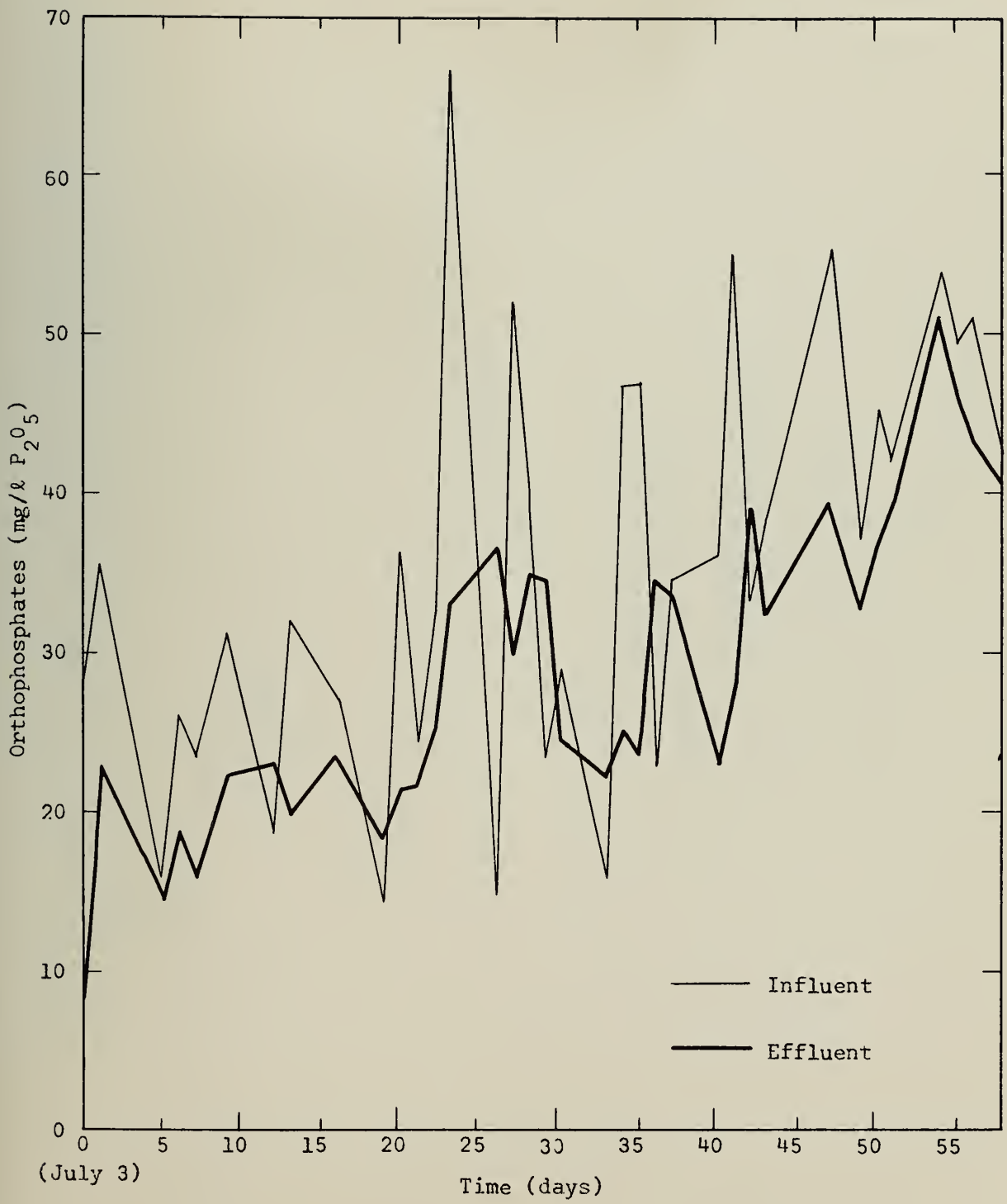


Figure 4. Orthophosphate Concentration in Column 1 (First Period)

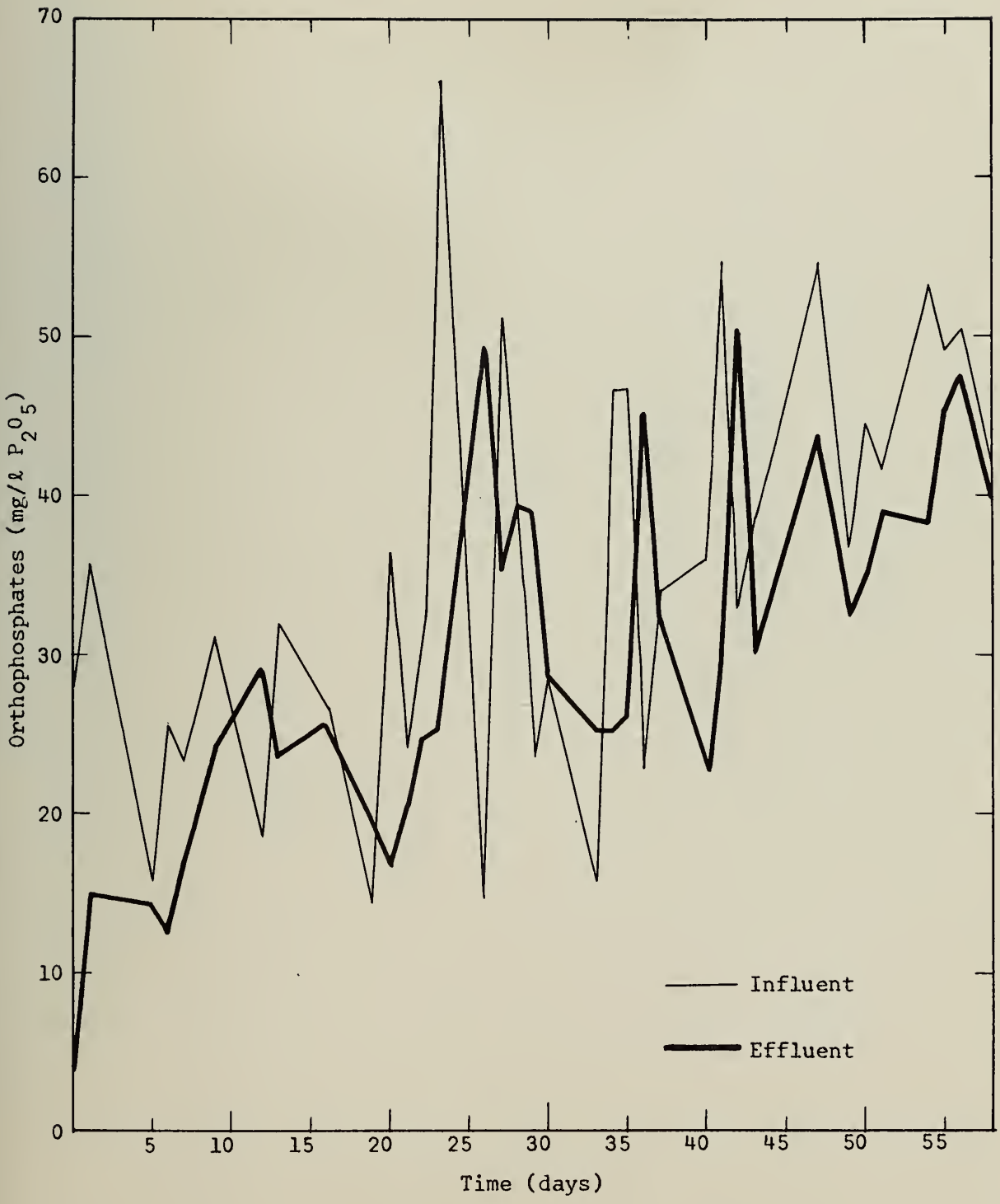


Figure 5. Orthophosphate Concentration in Column 2 (First Period)

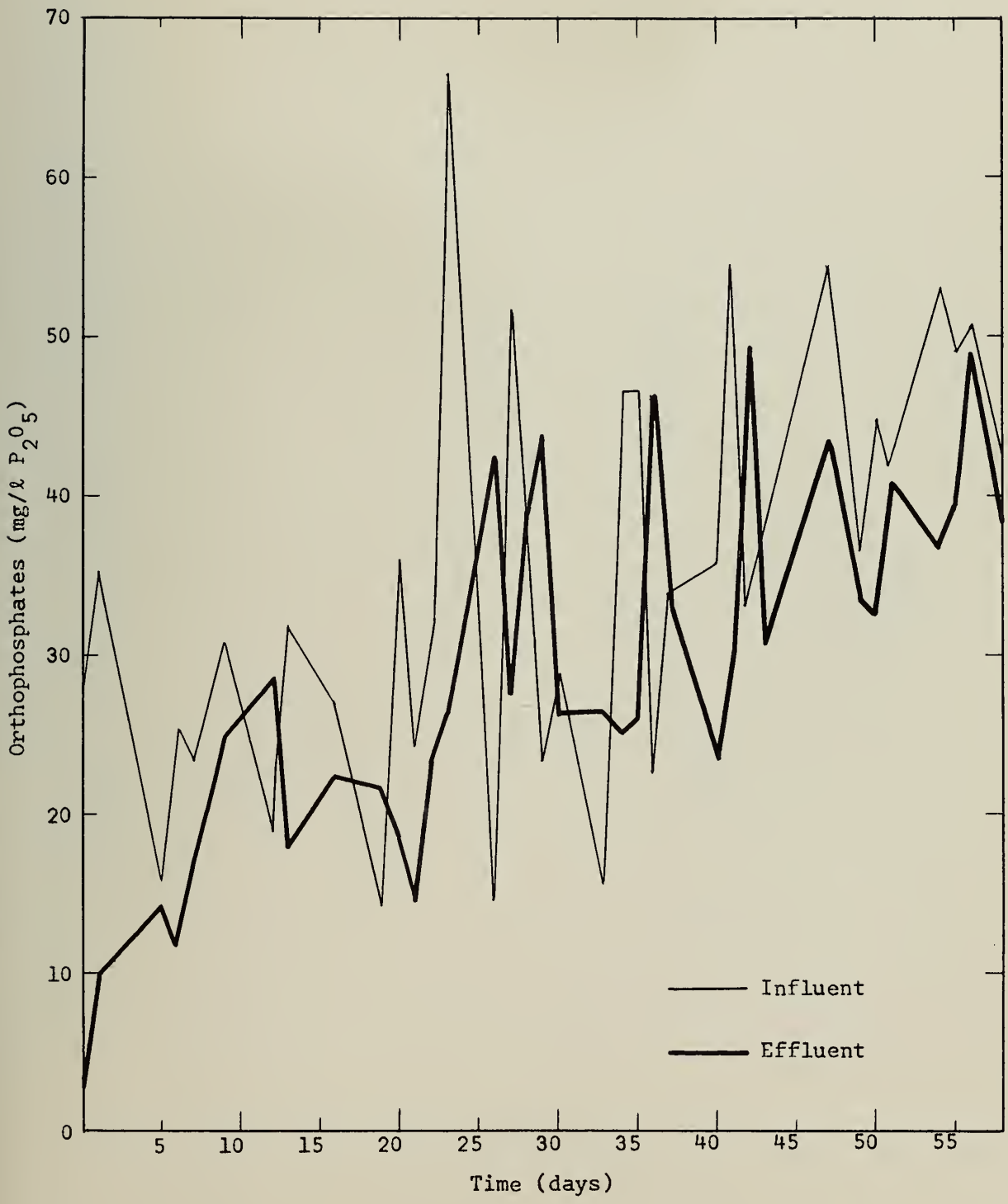


Figure 6. Orthophosphate Concentration in Column 3 (First Period)

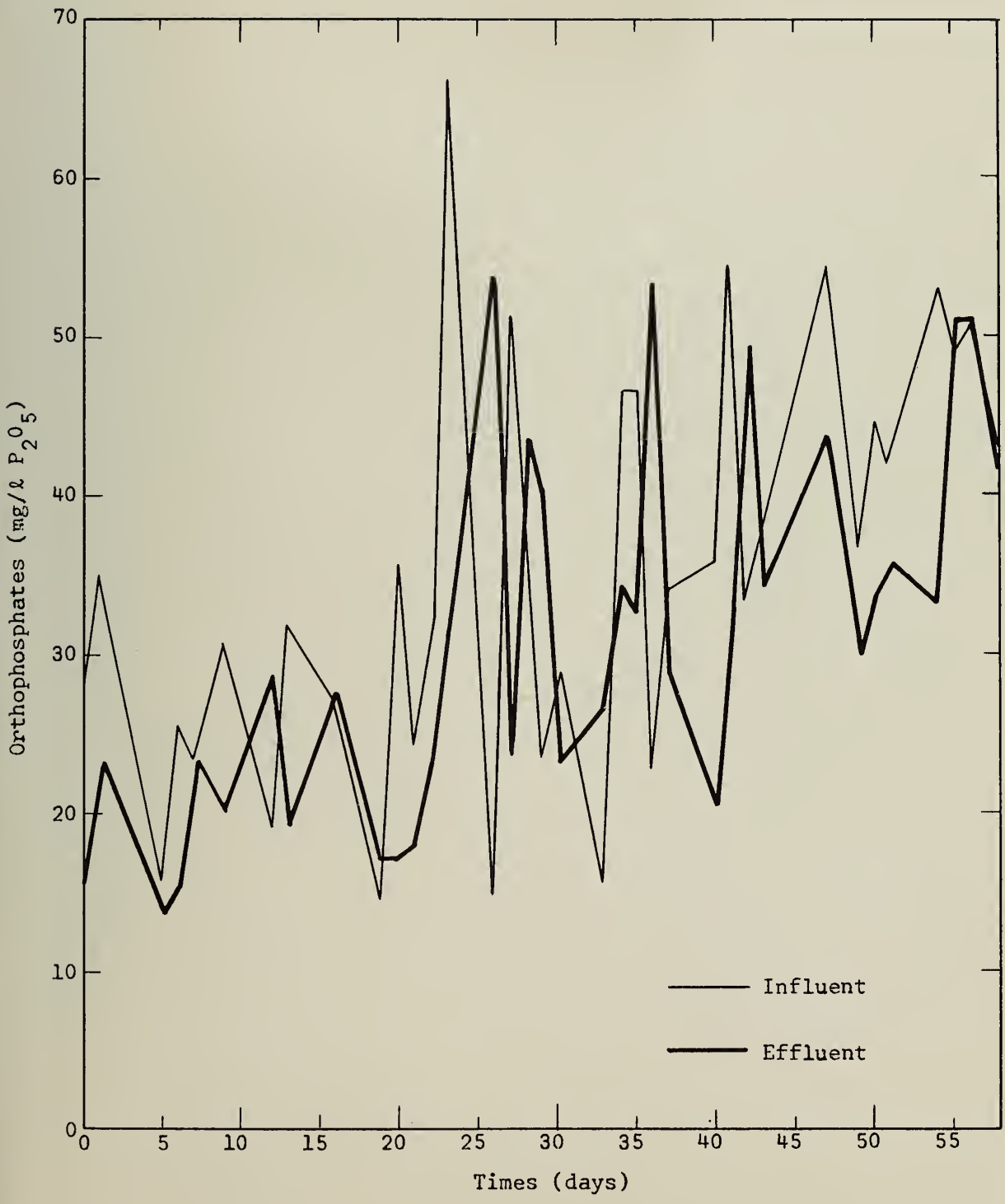


Figure 7. Orthophosphate Concentration in Column 4 (First Period)

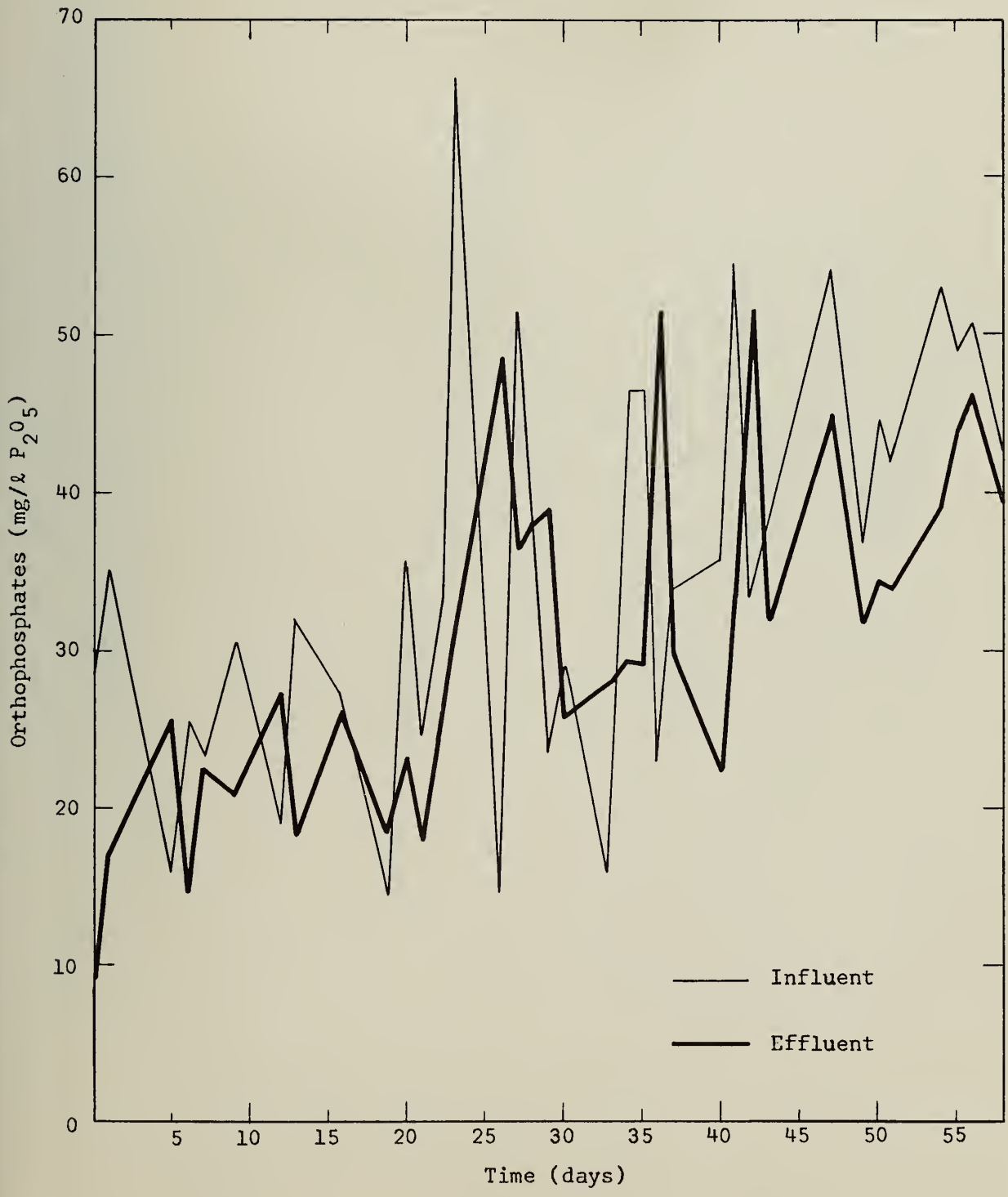


Figure 8. Orthophosphate Concentration in Column 5 (First Period)

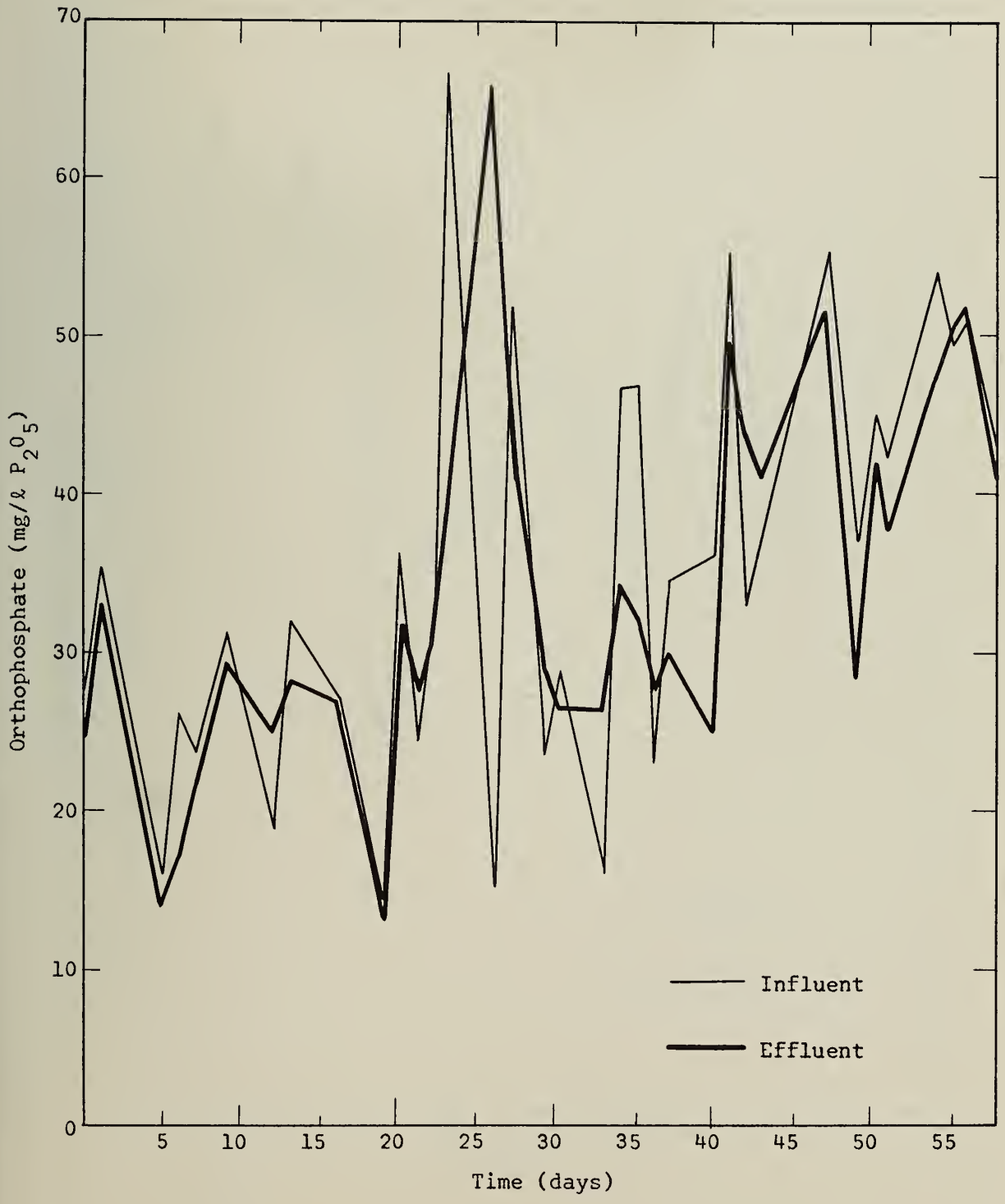


Figure 9. Orthophosphate Concentration in Column 6 (First Period)

Figure 10. Orthophosphate Concentration in Column 1 (Second Period)

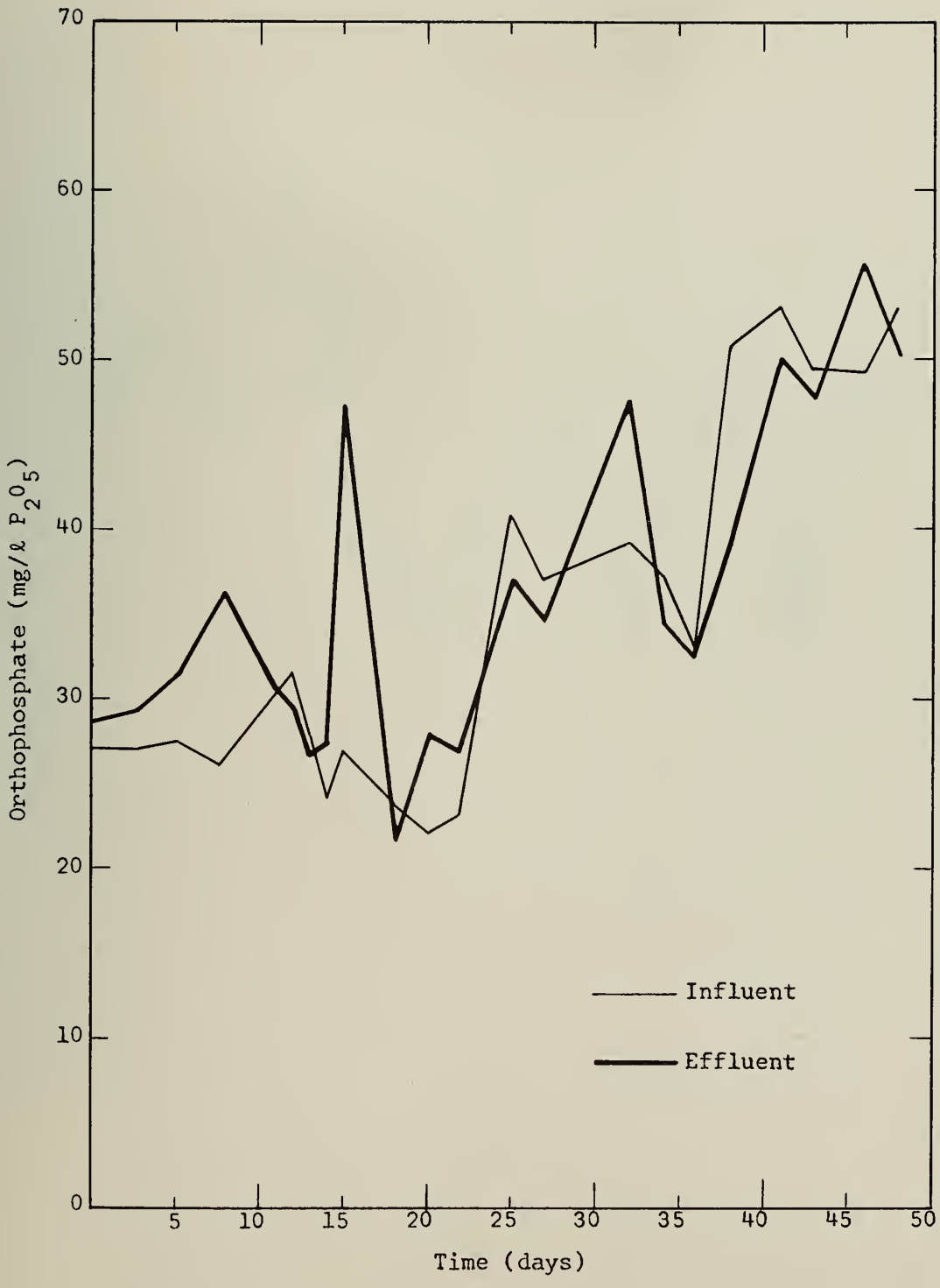


Figure 11. Orthophosphate Concentration in Column 2 (Second Period)

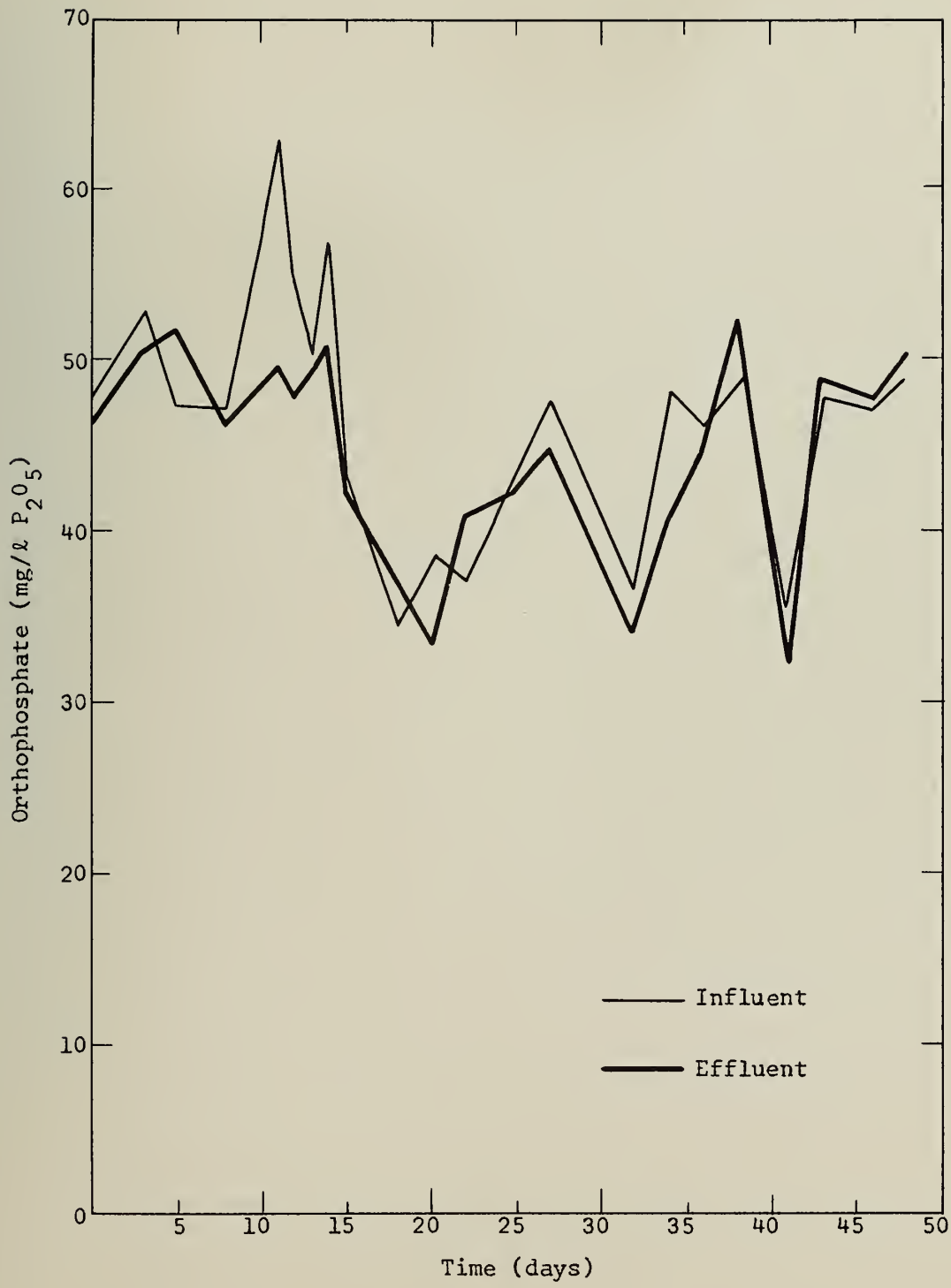


Figure 12. Orthophosphate Concentration in Column 3 (Second Period)

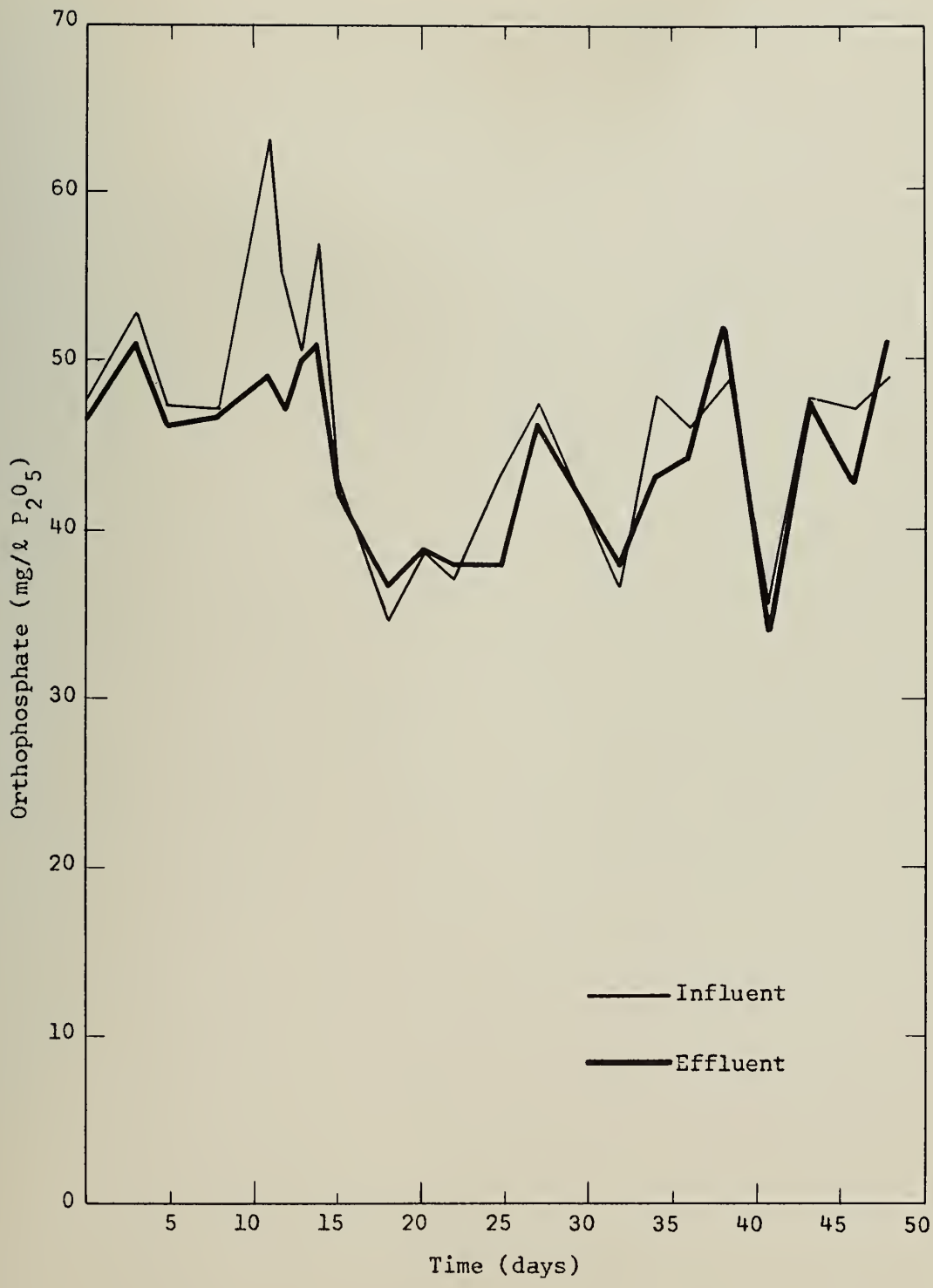


Figure 13. Orthophosphate Concentration in Column 4 (Second Period)

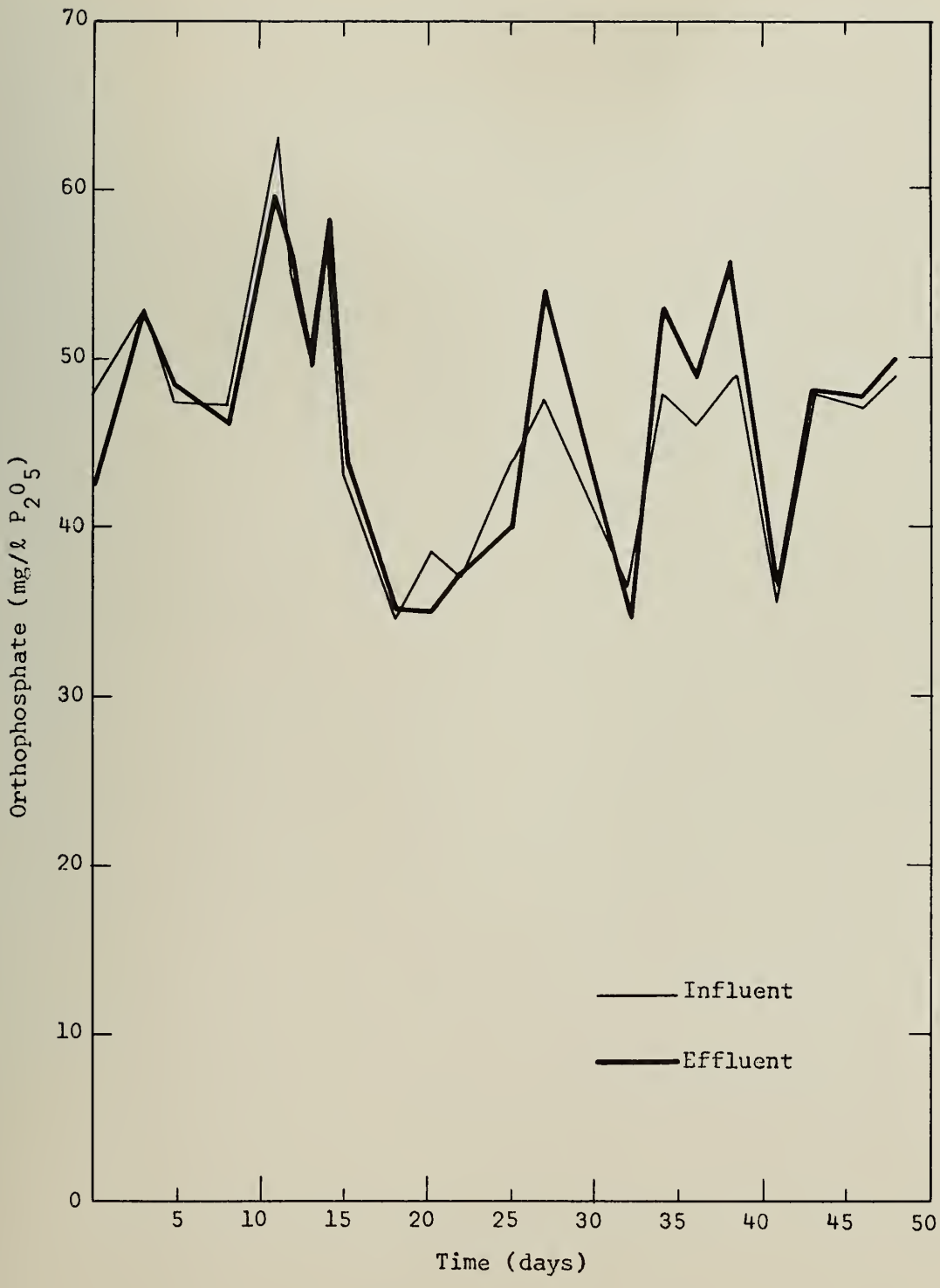


Figure 14. Orthophosphate Concentration in Column 5 (Second Period)

Figure 15. Orthophosphate Concentration in Column 6 (Second Period)

that all those days, which showed an increasing trend of orthophosphate concentration in the effluent, were on Mondays.

4.1.2. Condensed Phosphates

It was found that no great amount of condensed phosphates existed in the feed solution; the concentration ranged from 0 to 3.2 mg/ℓ with an average value of 1.83 mg/ℓ for the first period, and varied from 0 to 5.6 mg/ℓ with an average of 2.02 mg/ℓ for the second period. This amount was only about 4.5 percent of the orthophosphates or 4.2 percent of the total phosphates in the influent. The condensed phosphates have been reduced after passing through the columns. The removal has been calculated to vary from 22.3 percent to 67.8 percent. Figure 16 and Figure 17 are the bar-diagrams showing the removal of condensed phosphates.

4.1.3. Organic Phosphates

The organic phosphate was also reduced in the columns. The average concentration of organic phosphates in feed solution was found about the same as that of condensed phosphates. The rate of reduction ranged from 23.3 percent to 68.8 percent. The reduction in every column in the second period was greater than that in the first period except Column 2. The percent reduction in Column 2 decreased from 63.5 percent, the highest efficiency among the columns in the first period, to 35.4 percent, the lowest efficiency among the columns with sand medium. However, a synthetic feed containing higher organic phosphate concentration than regular sewage feed had been applied to Column 2 throughout the second period. The removal efficiency of Column 2 did not decrease as far as the reduction of organic phosphates in mg/ℓ was concerned. The bar-diagrams showing percentage reduction of organic phosphates have been shown in Figure 18 and Figure 19.

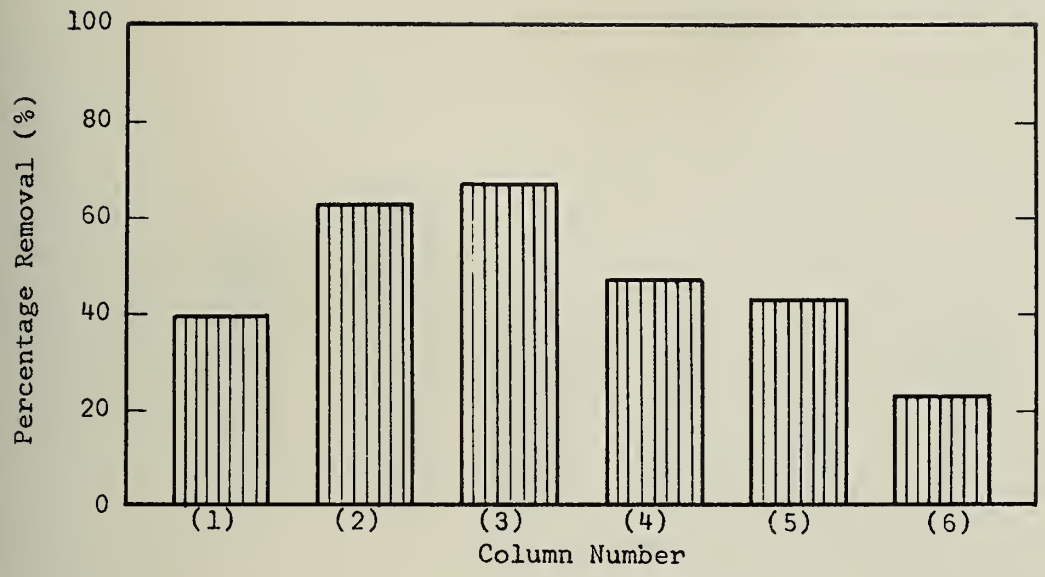


Figure 16. Percent Removal of Condensed Phosphates in First Period

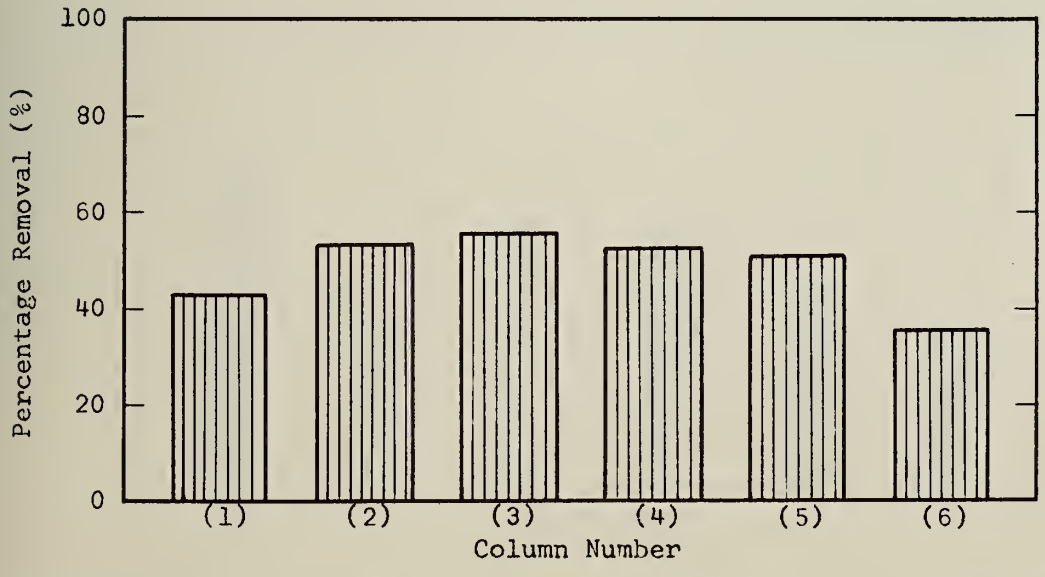


Figure 17. Percent Removal of Condensed Phosphates in Second Period

Figure 18. Percent Removal of Organic Phosphates in First Period

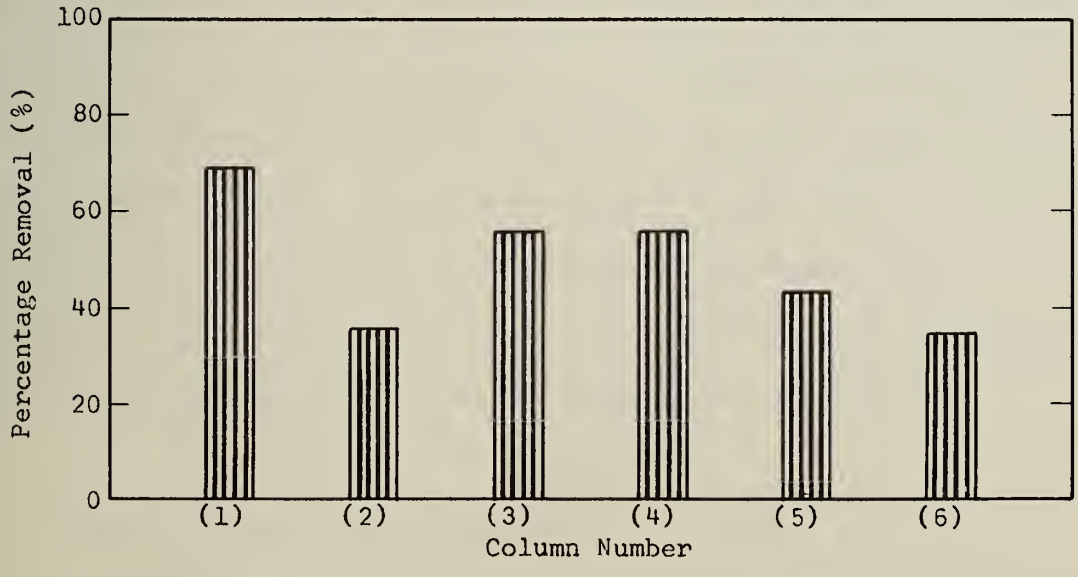


Figure 19. Percent Removal of Organic Phosphates in Second Period

4.1.4. Total Phosphates

The amount of total phosphate was taken as the sum of ortho-, condensed-, and organic-phosphates. The data have been presented in Table 17 through Table 20 (see Appendix C). Figure 20 shows the average concentration of total phosphates consisting of three forms of phosphates in influents and effluents. The average percentage removal of total phosphates in first period differed greatly from that in the second period. The difference was evident as shown in Figure 21. It is obvious that total phosphates were removed much greater in the first period than in the second period. The results of all forms of phosphate removal in percentage and standard deviation have been listed in Table 4.

4.2. Phosphate Removal versus Time

The data of percentage removal of total phosphates have been plotted versus time as shown in Figure 23 and Figure 24. It is evident that the phosphate removal in all columns decreased with time. The mechanisms of phosphate removal include both physical adsorption and biological assimilation. The high removal rate at first week in every column was mainly due to the greater initial adsorption rate. The low removal rate during second period was largely due to the biological uptake, since the adsorptive capacity is considered saturated during the first period. Figure 22 shows the amounts of total phosphates removed from feed solutions in every column.

4.3. Phosphate Removal versus Feeding Rate

It has been found that the reduction rate of total phosphates is a function of loading rate. The greater the amount of sewage fed the lower the concentration of phosphates removed. Column 3 which had a least loading

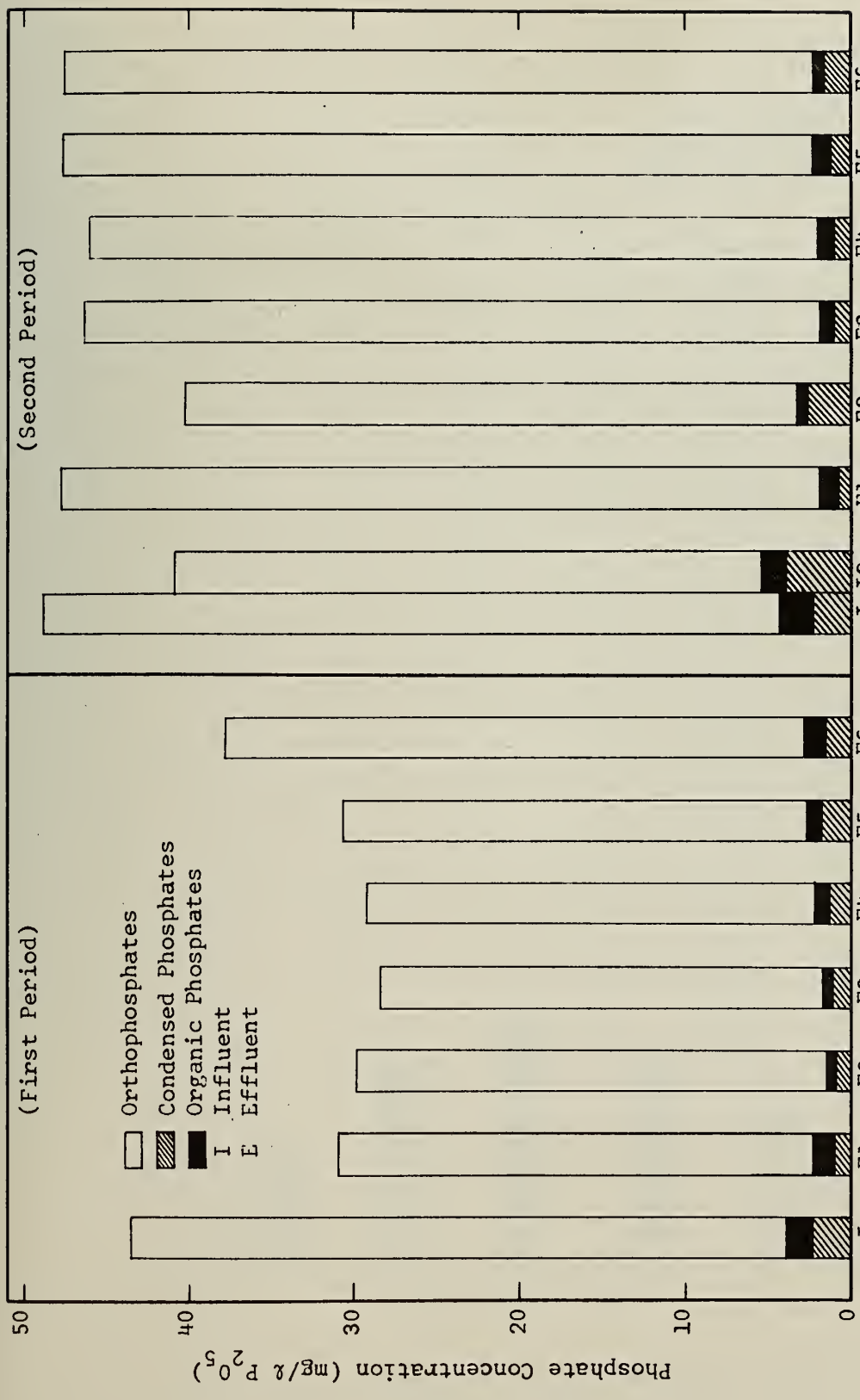


Figure 20. Average Concentration of Total Phosphates in Column Influents and Effluents

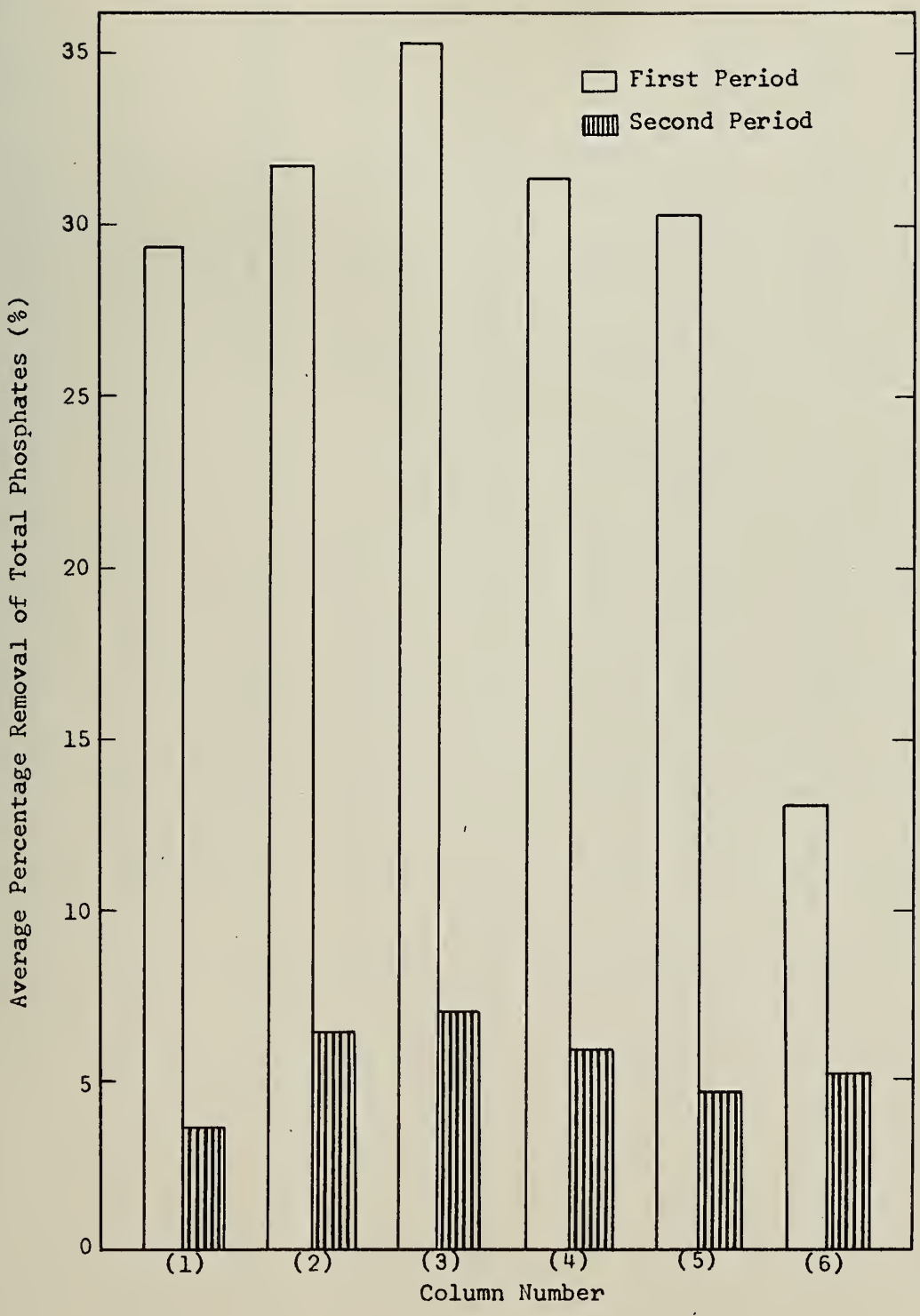


Figure 21. Comparison of Total Phosphate Removal Between First and Second Period

Table 4

AVERAGE AND STANDARD DEVIATION DATA OF PHOSPHATE REMOVAL BY SAND COLUMNS

Column No.	1		2		3		4		5		6		Influent	
Period	I	II	I	II	I	II	I	II	I	II	I	II	I	II
Ortho-Phosphate:														
Average conc.,mg/ℓ	28.86	45.89	28.52	37.03	26.93	44.59	27.26	44.11	27.97	45.44	35.08	45.52	39.63	44.88 (35.67)*
Standard Devia.,mg/ℓ	14.50	-	18.25	-	17.52	-	14.35	-	15.90	-	12.05	-		
Percent Removal %	27.3	0	28.2	0	32.2	0.7	31.3	1.7	29.6	0	11.6	0		
Condensed-Phosphate:														
Average conc.,mg/ℓ	1.10	1.16	0.67	0.61	0.59	0.90	0.96	0.96	1.03	0.98	1.42	0.72	1.83	2.02 (1.31)*
Standard Devia.,mg/ℓ	0.96	1.17	0.81	0.60	0.80	0.88	0.98	1.10	1.07	1.07	1.10	0.89		
Percent Removal %	39.9	42.6	63.4	53.4	67.8	55.4	47.6	52.5	43.7	51.5	22.3	64.3		
Organic-Phosphate:														
Average conc.,mg/ℓ	0.97	0.65	0.74	2.54	0.94	0.93	1.11	0.93	1.56	1.19	1.35	1.36	2.03	2.08 (3.93)*
Standard Devia.,mg/ℓ	0.75	1.15	0.66	1.71	1.09	1.32	1.86	1.27	1.72	1.22	1.57	1.26		
Percent Removal %	52.3	68.8	63.5	35.4	53.7	55.3	45.3	55.3	23.3	42.8	33.5	34.6		
Total Phosphate:														
Average conc.,mg/ℓ	30.93	47.70	29.93	40.18	28.46	46.42	29.33	46.00	30.56	47.61	37.85	47.60	43.49	48.98 (40.91)*
Standard Devia.,mg/ℓ	16.7	4.12	19.2	5.26	18.9	5.04	15.3	5.39	15.8	4.38	9.2	5.05		
Percent Removal %	29.28	3.65	31.75	6.42	35.26	6.95	31.40	5.83	30.15	4.51	12.98	5.18		

*Synthetic Feed

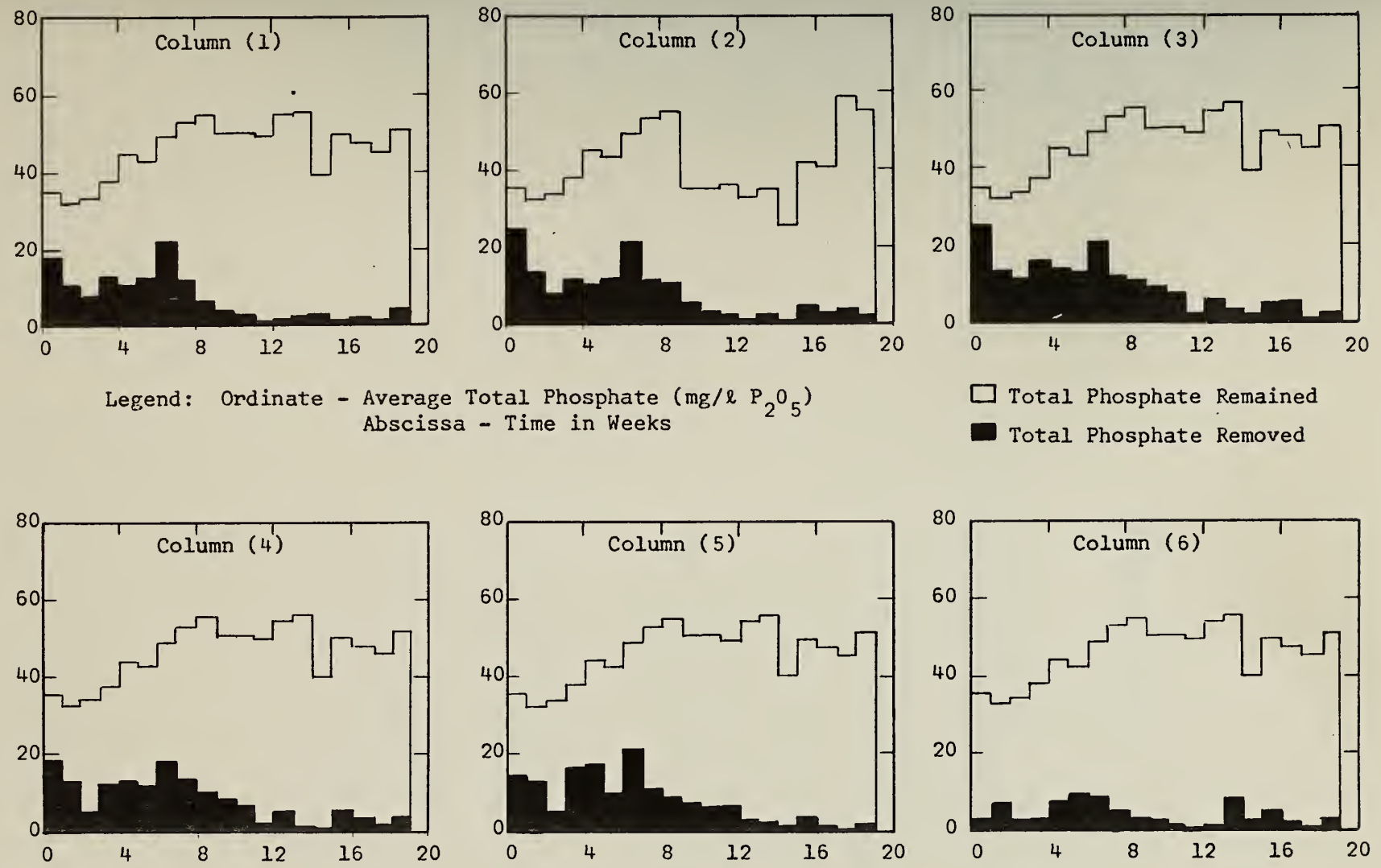


Figure 22. Average Concentration of Total Phosphates Removed by the Columns

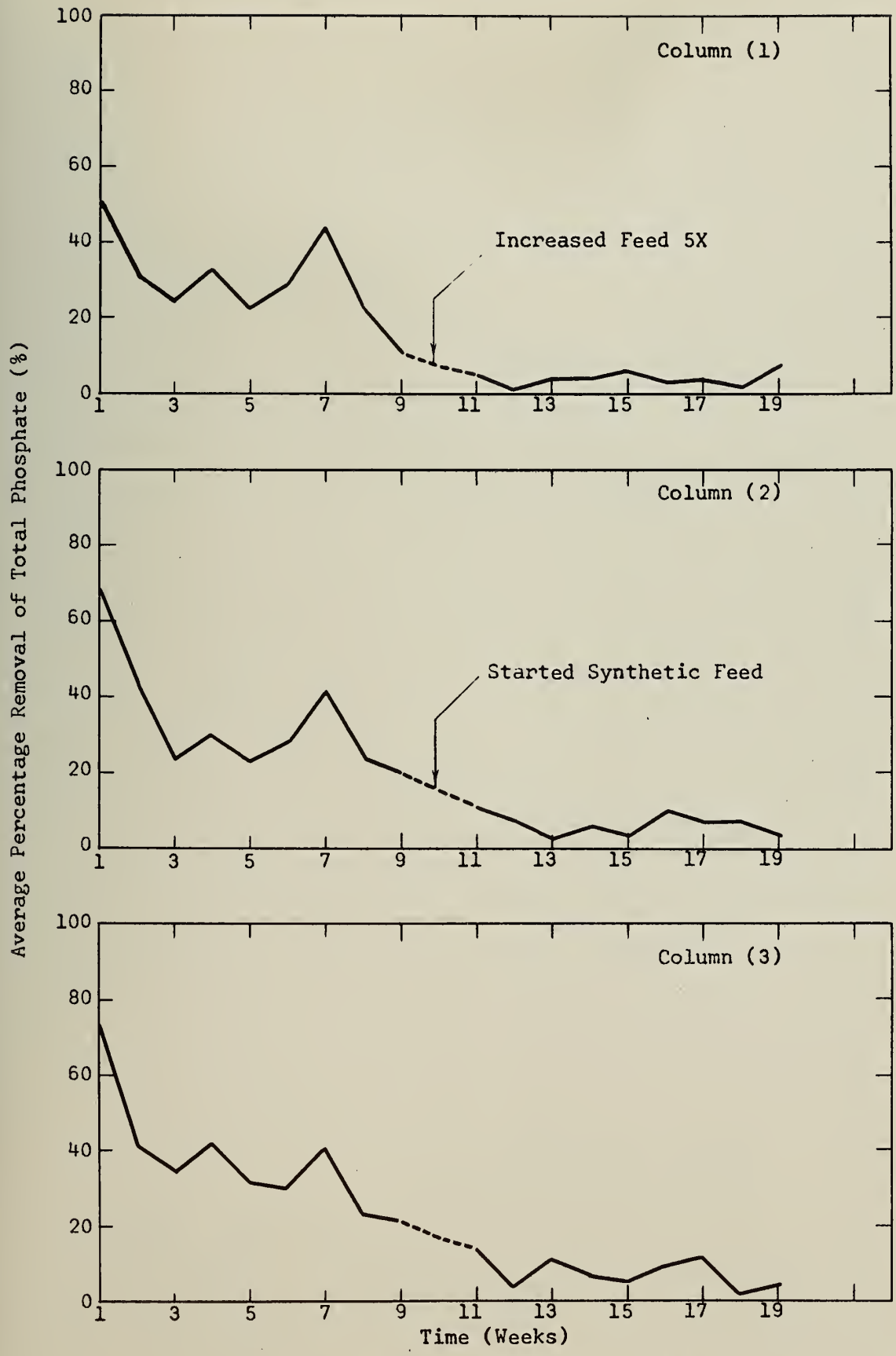


Figure 23. Total Phosphate Removal versus Time (I)

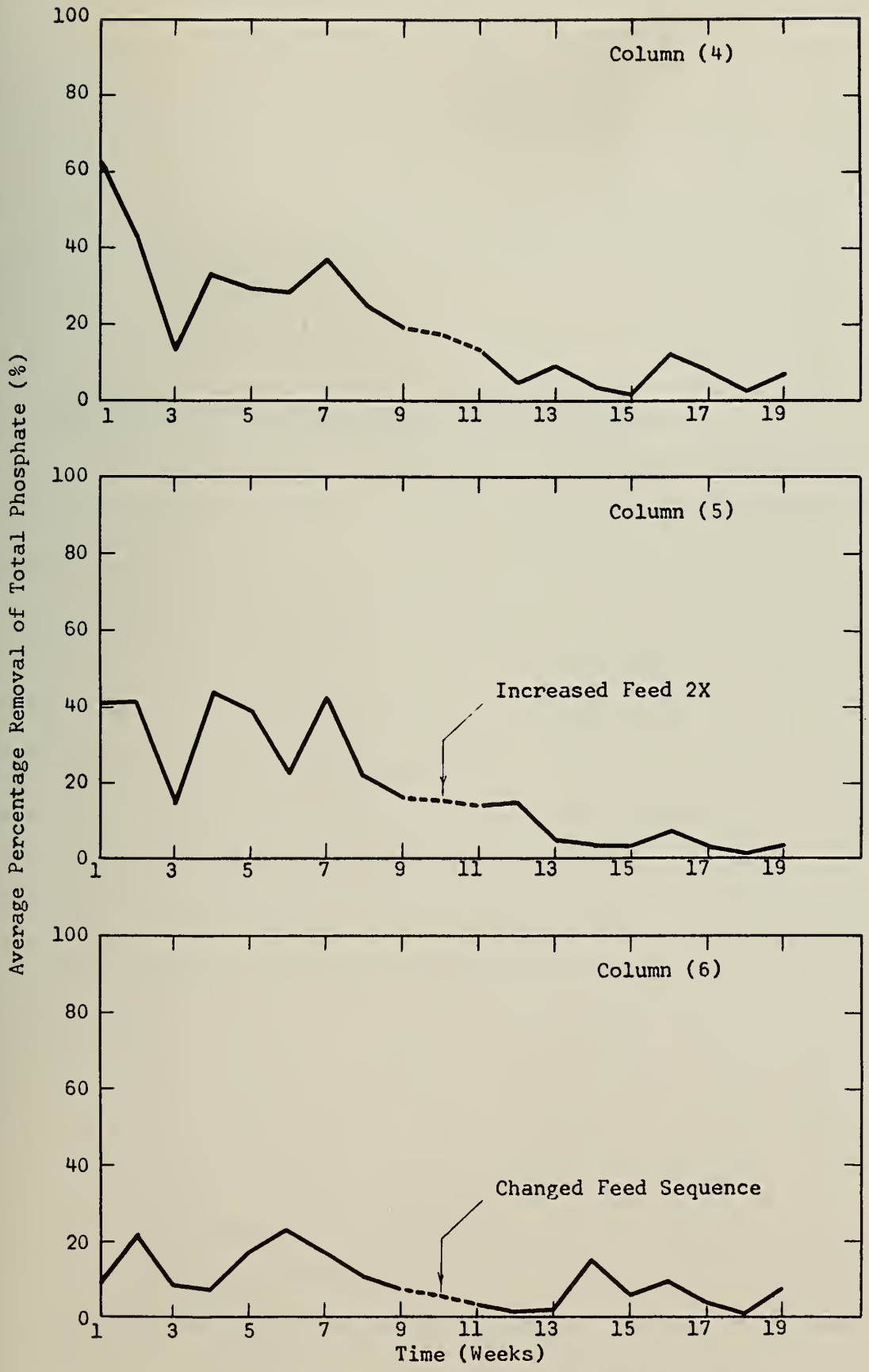


Figure 24. Total Phosphate Removal versus Time (II)

performed best in the removal of phosphate, while column 6 which received a highest load did a poor job. Figure 25 shows the relationship between feeding rate and the percent removal of total phosphates of the columns. The curves indicate that the percent removal of phosphates decreased with increasing dose rate. The dose rate is expressed in terms of phosphate loading which is calculated on the basis of average concentration of phosphates in the feed solution.

4.4. Phosphates Removed by Adsorption and Assimilation

Cumulative phosphate removal of the six columns in nineteen weeks has been calculated on the basis of weekly average removal of individual columns. The total quantity of phosphates removed in 19 weeks ranged from 7852 mg to 2582 mg or, if expressed in terms of mg of P_2O_5 removed by each gram of sand, varied between 0.21 to 0.65 with an average of 0.36 mg of P_2O_5/gm of sand. The cumulative removal of phosphates was found to be positively increased with hydraulic feed loading. But this is of less significance as far as the removal efficiency is concerned. Although Column 5 received a higher loading and was the most successful in the cumulative removal, its efficiency of percent removal was not an excellent one. We are more interested in the percent removal efficiency of the columns. Figure 26 to Figure 31 show the cumulative removal of total phosphates versus time. In these figures, the total phosphate removal is plotted as ordinate and the time as abscissa. The resulting curve shows that its slope is steeper in the first period than in the second period. This also indicates that the removal rate was greater in the first period than in the second period. There is an attempt to separate the amount of phosphates removed by physical adsorption and by biological assimilation in the light of the curve so plotted. Assuming that phosphate

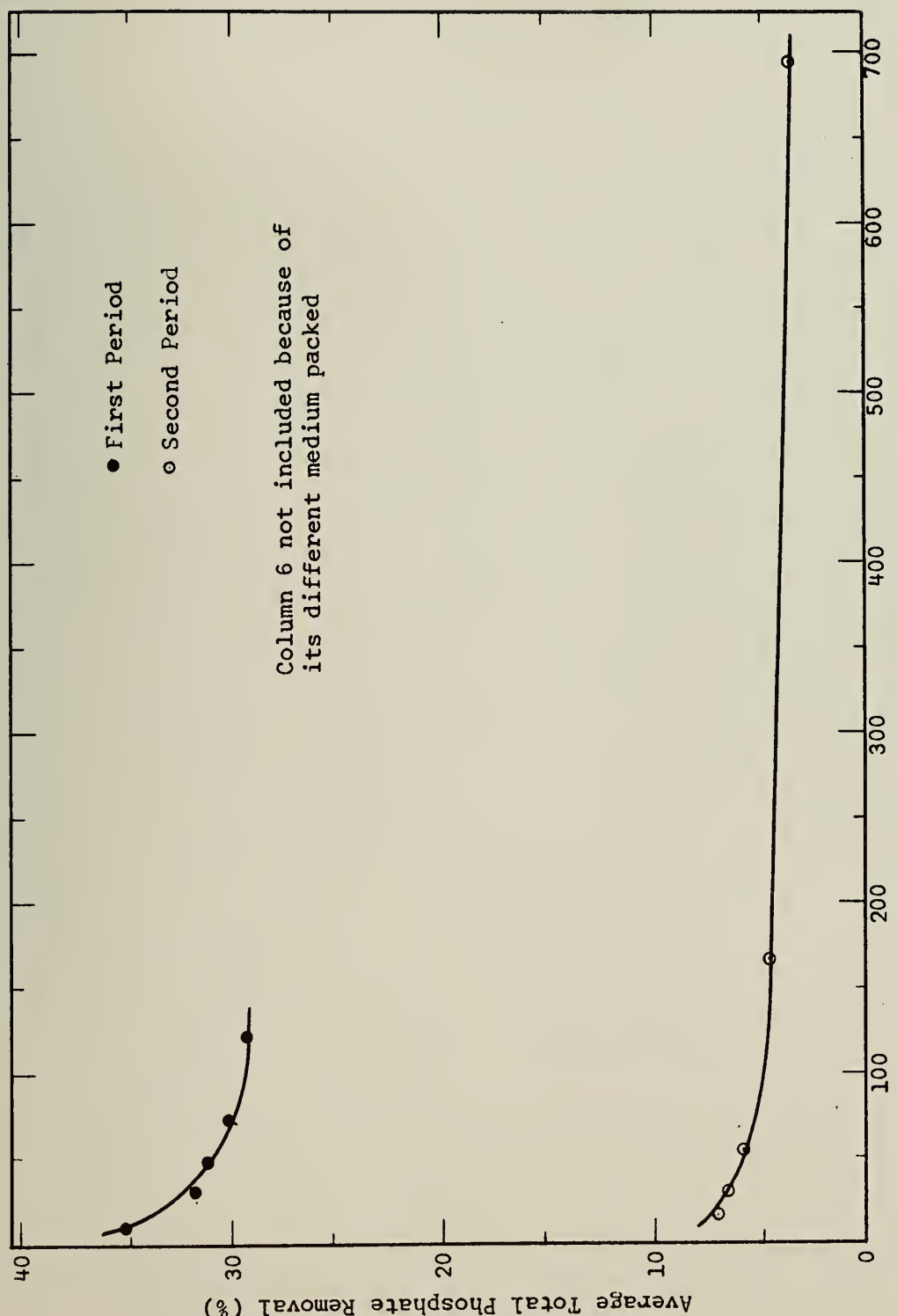


Figure 25. Phosphate Removal versus Dose Rate

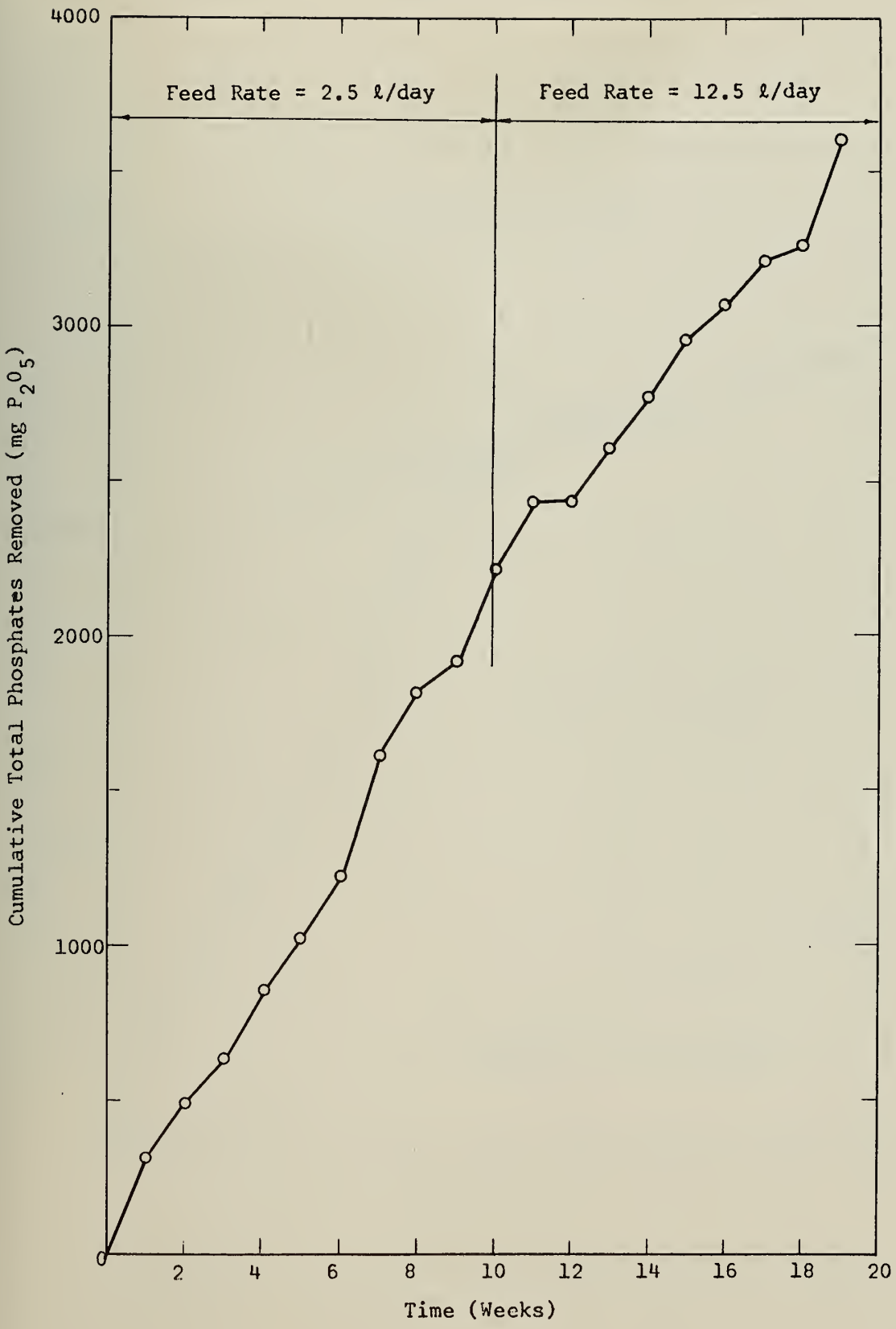


Figure 26. Cumulative Total Phosphate Removed by Column 1

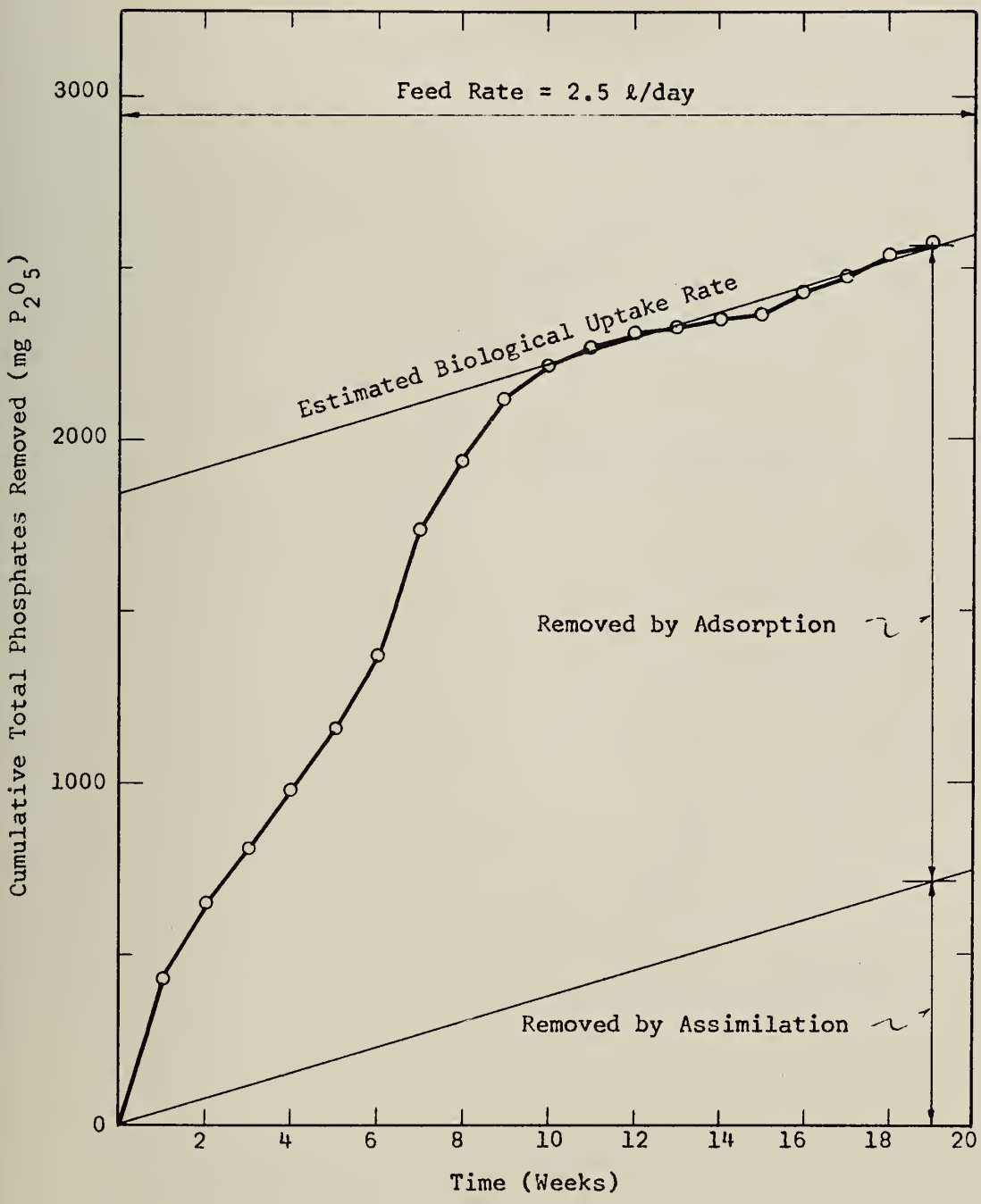


Figure 27. Cumulative Total Phosphate Removal by Column 2

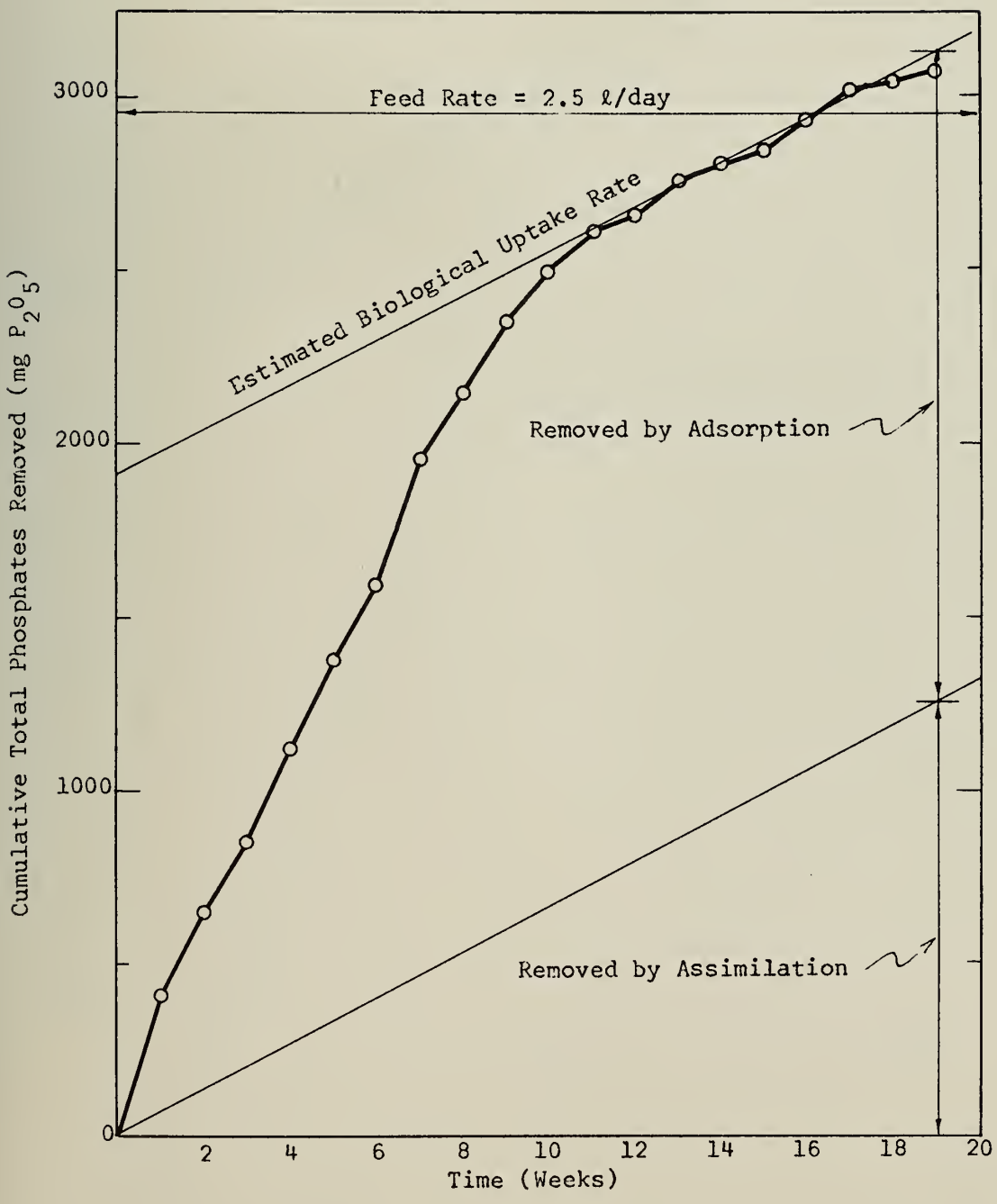


Figure 28. Cumulative Total Phosphate Removal by Column 3

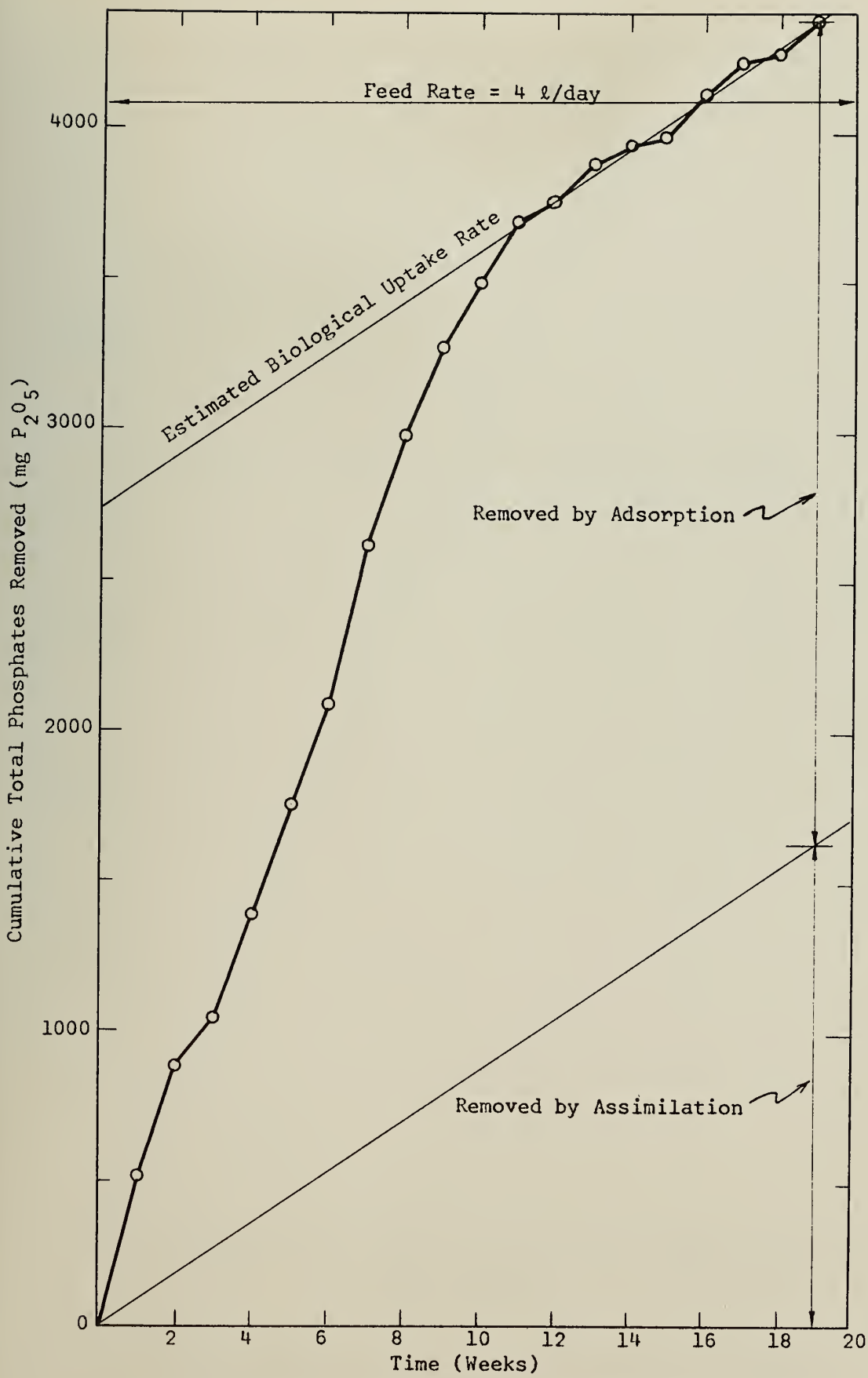


Figure 29. Cumulative Total Phosphate Removal by Column 4

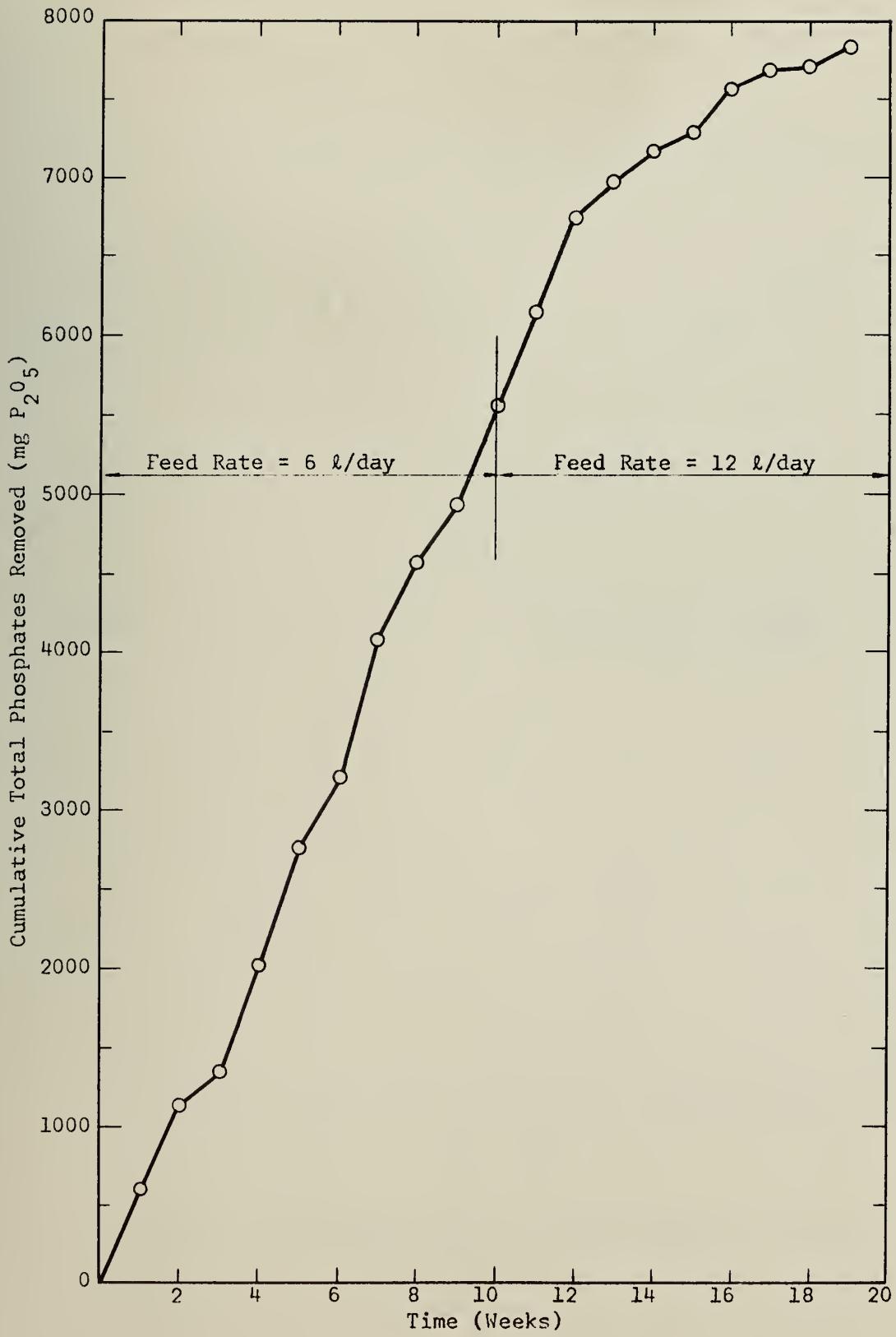


Figure 30. Cumulative Total Phosphate Removal by Column 5

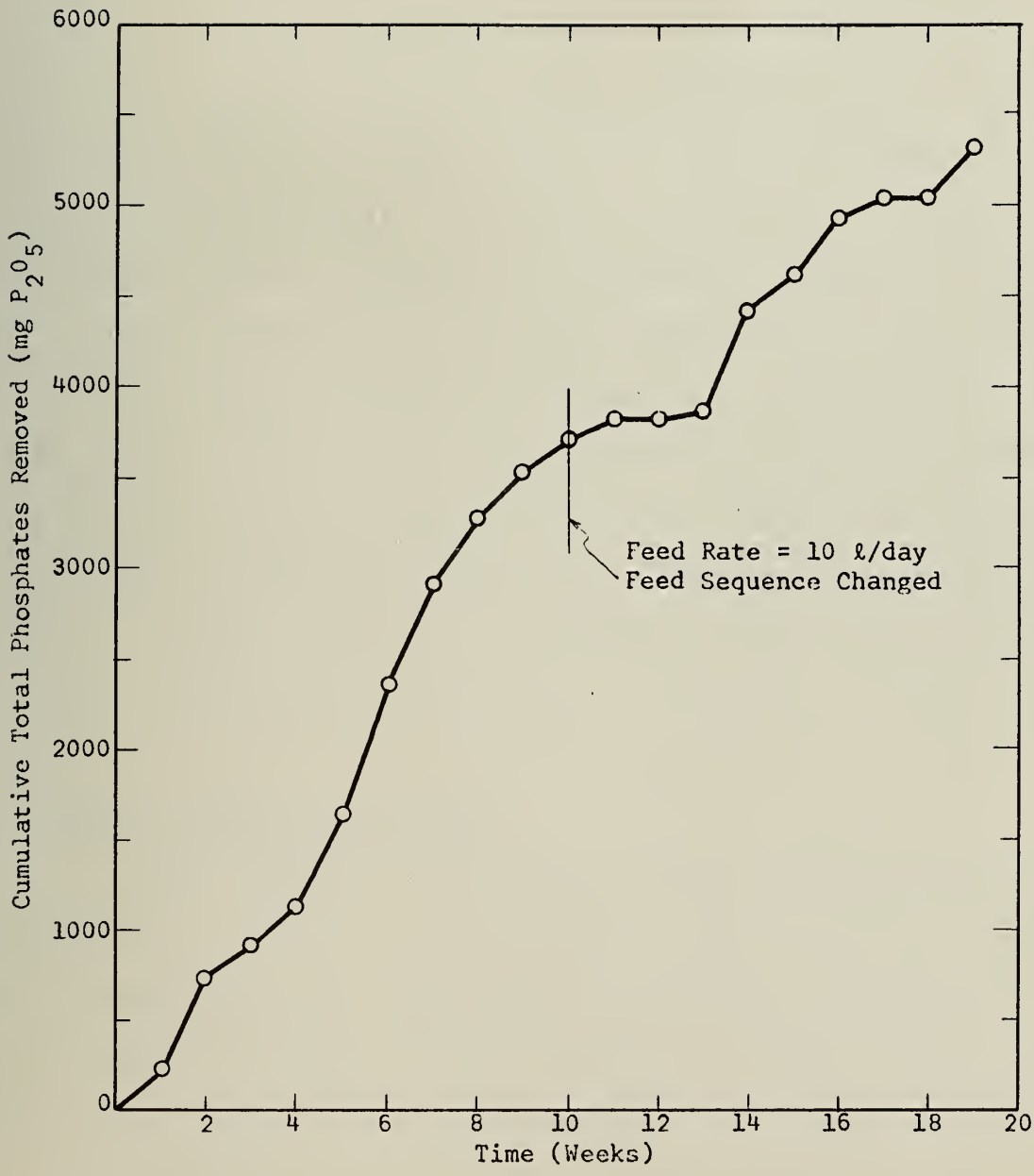


Figure 31. Cumulative Total Phosphate Removal by Column 6

removal during the first period was due to the combination of physical adsorption and biological assimilation and that in second period was due to biological uptake rather than adsorption, if the slope of the curve in the second period portion can be extended to vertical axis, the intercept on ordinate will then indicate the total amount of phosphates removed by adsorption. If a parallel line is drawn through the origin, its ordinate will give the amount of phosphates removed by biological assimilation at the period the ordinate stands. However this method was only applied acceptably to Columns 2, 3 and 4. Other columns could not be treated successfully with this method because their operating conditions were changed in the second period. For instance, the feed rate of Column 1 was increased five times in the second period; although its percent removal efficiency was considerably lower than in the first period its cumulative removal curve did not decrease the slope after the feed rate changed. Therefore, only Columns 2, 3 and 4 were taken for this study. The result is presented in Table 6.

4.5. Operating Condition of Columns

In order to grow active microbial cultures on the column medium so that the biological activity could be developed before routine feeding schedule started, a synthetic sewage solution containing settled sewage, glucose, ammonium chloride and phosphate buffer was used for seeding of the columns. The seeding was carried on in a four-day period. Considerable COD removals were obtained thereafter, so the feeding schedule as mentioned in Table 3 was performed continuously until the end of the investigation when the columns were opened. COD test was done very often. Table 5 gives the percent removal of COD of the various columns. The result indicates that a considerable amount of organic materials were removed by the columns. This also means that the columns were operated under the condition of biological activity.

Table 5

PERCENT COD REMOVAL BY SAND COLUMNS

Column No.	1		2		3	4	5		6	
Medium	Sand		Sand		Sand	Sand	Sand		Gravel	
Feed Load l/day	2.5	12.5	2.5	2.5*	2.5	4.0	6.0	12.0	10.0	10.0**
Average COD Removal, %	29.9	19.0	44.6	79.3	54.4	42.8	36.7	28.4	23.2	20.2
Standard Deviation, %	21.0	14.2	22.2	14.4	14.0	13.4	17.8	16.6	15.4	16.2
Date***	A	B	A	B	A & B	A & B	A	B	A	B

*Synthetic Feed
**Feeding sequence changed
***A = First Period (7/3/63 to 9/9/63)
B = Second Period (7/9/63 to 11/11/63)

Table 6

CUMULATIVE REMOVAL OF TOTAL PHOSPHATES IN NINETEEN WEEKS

Column No.	Total Amount of P_2O_5 Removed mg	Removed by Adsorption		Removed by Assimilation		Phosphates Removed per Gram of Sand mg	Hydraulic Feed Load l/day	Average Phosphate Loading mg P_2O_5/day
		mg	%	mg	%			
1	3609	--	--	--	--	0.30	Changed*	Changed*
2	2582	1850	71.5	732	28.5	0.21	2.5	105
3	3078	1900	61.8	1178	38.2	0.25	2.5	116
4	4351	2730	62.7	1621	37.3	0.36	4.0	185
5	7852	--	--	--	--	0.65	Changed*	Changed*
6	5313	--	--	--	--	0.39	Changed*	Changed*

*Feeding Load Changed in the Second Period (See Table 3)

4.6. Elution of Columns

After running nineteen weeks on phosphate determination, it was decided to finish the routine experiment and to open the columns to examine the medium conditions. Before dismantling the columns, 10 to 12 liters of tap water were added to each column to see if the phosphates previously retained in the column could be sloughed off and carried out with the elution effluent. Four effluent samples were collected for each column. The grab samples were so collected that they could represent the continuity of the elution curve after their phosphate concentrations were determined. Figure 32 gives the elution curves of the columns. Very similar curves were obtained for the columns with sand medium. Column 6 with a different type of medium showed a distinctive curve. The elution curves indicate that high concentration of phosphates was found in the first liter of the total elution volume, and as the volume of elution extended the phosphate concentration decreased sharply. The area under the curve equals to the amount of phosphates elutriated from the column by tap water. The quantity of phosphates eluted from each column has been calculated from the elution curve and listed in Table 7.

The elution of Column 1 was not performed because the decision was not made until the column was dismantled. Column 4 and Column 5 were fed again after being eluted. A special investigation was made to see the phosphate removal efficiency of these two columns after elution. Surprisingly, the result showed that the percent removal after elution was as high as 81.5 percent in Column 4 and 89.0 percent in Column 5. The data have been given in Table 8. Since the result of elution was quite interesting, a further study was put on Column 5 in which a second elution was made after ten days from first elution. The percent removal after second elution was almost the same as in the first elution. Table 9 presents this data vividly.

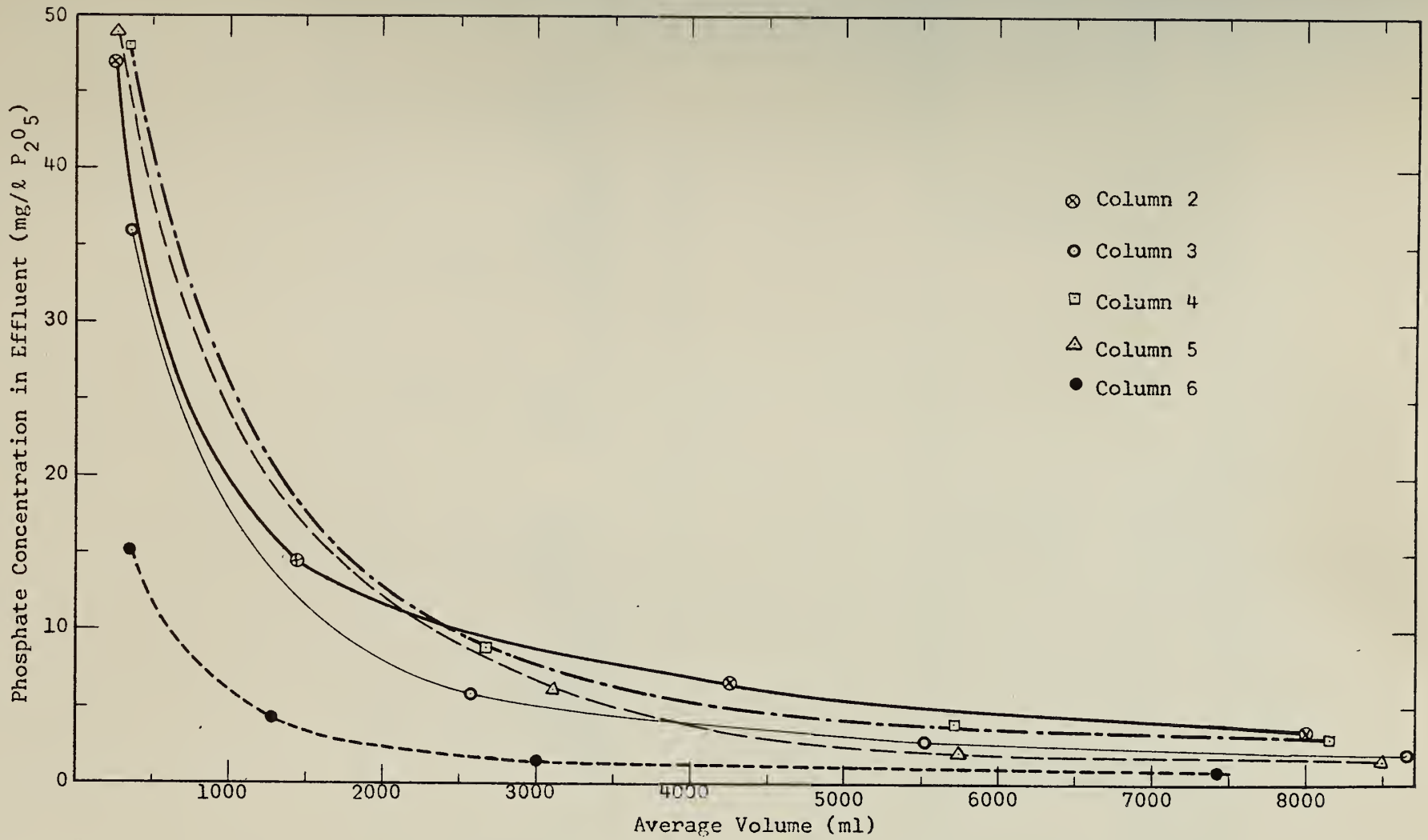


Figure 32. Elution of Columns with Tap Water

Table 7

TOTAL PHOSPHATES REMOVED AND AMOUNT THAT CAN BE ELUTED

Column No.	Total Phosphates Removed by Column mg P_2O_5	Phosphates Eluted by Tap Water mg P_2O_5	Phosphate Feed Load mg P_2O_5/Day	
			A	B
1	3609	--	109	613
2	2582	88.8	109	102
3	3078	66.8	109	123
4	4351	95.5	174	196
5	7852	85.1	261	588
6	5313	22.5	435	490

A = First Period
B = Second Period

Table 8

PHOSPHATE REMOVAL BEFORE AND AFTER ELUTION

Column No.	Before Elution			After Elution		
	Phosphate Content		Percent Removal	Phosphate Content		Percent Removal
	Influent mg/ℓ	Effluent mg/ℓ	%	Influent mg/ℓ	Effluent mg/ℓ	%
4	41.8	39.6	5.2	48.7	9.0	81.5
5	48.6	42.5	12.6	42.8	4.7	89.0
5*	54.8	53.7	2.1	51.0	6.0	88.2

*Second Elution

Table 9

ELUTION DATA OF COLUMN 5

Day	Phosphate Con. in Influent mg/ℓ	Phosphate Con. in Effluent mg/ℓ	Percent Removal %	Remark
0	48.6	42.5	12.6	
1	42.8	4.7	89.0	Just after first elution
2	51.0	24.0	52.9	
4	50.5	39.0	23.5	
5	50.0	42.2	15.6	
6	56.0	47.7	14.8	
8	59.3	51.3	13.5	
10	54.8	53.7	2.1	
11	51.0	6.0	88.2	Just after second elution
13	38.8	25.5	34.2	
14	32.8	20.7	36.9	
15	31.0	22.6	27.1	
18	25.0	20.7	17.2	

Elution performed on 1st and 11th day.

4.7. Investigation of Column Medium at the End of Experiment

At the end of the experiment, each column was dismantled in order to investigate the characteristics of the medium. It was decided to determine the moisture content, volatile solids, and bacterial density for the medium in each column. Four samples taken from different depths of each column were analyzed. Bacterial counts were made on the wash solution of a known amount of medium sample. These data will give an idea of the biological activities in the columns. Volatile solids provide a measure of organic substances existing as slime on the medium particles. The slime is the mass of bacteria; therefore the volatile solids should check with bacterial data theoretically. The results of these items have been listed in Table 10 and their corresponding relations have been drawn in Figure 33. From this plotting, it is evident that moisture content of sand increased with depth in all columns except Column 6. The sand in the bottom of column had highest moisture content because of the poor drainage near the bottom. Column 6, packed with pea gravel, showed a moisture content nearly constant at all depths because the coarse layers did not show much variation. Bacterial counts did not appear to correlate very well with volatile solids. Column 6 gave an excessive high value of volatile solids because the gravel expelled CO_2 when fired at 600°C in the determination process.

Table 10

VARIATION OF MOISTURE, VOLATILE SOLIDS AND BACTERIA COUNTS OF COLUMNS WITH DEPTH OF SAND

Column No.	Experiment Items	Sample 1	Sample 2	Sample 3	Sample 4
(1)	Sampling Point (cm from bottom)	92	71	45	6
	Moisture (%)	2.100	3.085	3.000	15.830
	Volatile Solid (gm/gm of sand)	0.816	0.697	0.719	0.779
	Bacteria Count (no./gm of sand)	0.84×10^5	0.25×10^5	0.09×10^5	0.59×10^5
(2)	Sampling Point (cm from bottom)	94	72	43	3
	Moisture (%)	3.186	3.522	3.539	11.846
	Volatile Solid (gm/gm of sand)	0.803	0.726	0.782	0.726
	Bacteria Count (no./gm of sand)	2.1×10^5	1.2×10^5	0.7×10^5	0.4×10^5
(3)	Sampling Point (cm from bottom)	94	71	44	5
	Moisture (%)	4.910	5.565	4.850	15.990
	Volatile Solid (gm/gm of sand)	0.721	0.604	0.744	0.727
	Bacteria Count (no./gm of sand)	0.5×10^5	0.76×10^5	0.57×10^5	0.45×10^5
(4)	Sampling Point (cm from bottom)	90	68	35	5
	Moisture (%)	2.789	3.405	4.273	13.643
	Volatile Solid (gm/gm of sand)	0.765	0.711	0.712	0.790
	Bacteria Count (no./gm of sand)	3.4×10^5	2.9×10^5	0.82×10^5	0.68×10^5
(5)	Sampling Point (cm from bottom)	92	68	41	11
	Moisture (%)	3.925	4.029	4.291	14.946
	Volatile Solid (gm/gm of sand)	0.829	0.715	0.705	0.690
	Bacteria Count (no./gm of sand)	0.32×10^5	0.78×10^5	2.20×10^5	0.60×10^5
(6)	Sampling Point (cm from bottom)	94	66	39	5
	Moisture (%)	5.807	5.127	5.123	5.842
	Volatile Solid (gm/gm of sand)	2.082	2.334	1.832	1.750
	Bacteria Count (no./gm of sand)	0.36×10^5	0.16×10^5	0.10×10^5	0.11×10^5

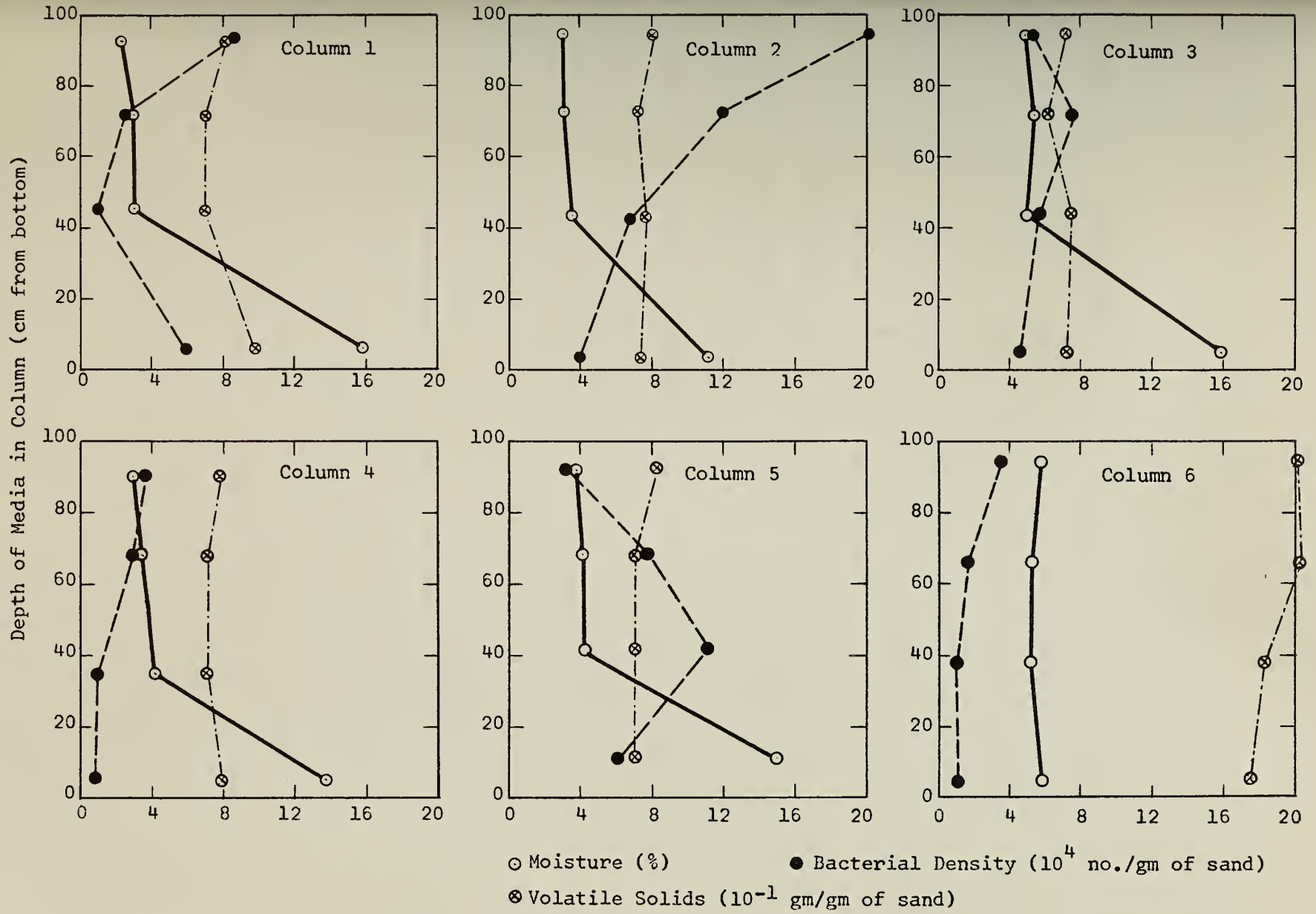


Figure 33. Evaluation of Moisture, Volatile Solids and Bacterial Density in Sand Columns

CHAPTER 5: DISCUSSION OF THE RESULTS

5.1. Phosphates Removed by Sand Columns

The results obtained in this experiment have shown that a minor but significant amount of phosphates in all forms has been removed by the sand columns under study. Greater phosphate removal was observed in the early dates, probably due to the physical adsorption on medium particles rather than the pure biological uptake of growing organisms. The bacterial growths in this early period would not have been well developed, i.e., the bacterial population was still too low to cause large scale phosphate removal resulting from their utilization of phosphates as nutrients.

Orthophosphates were removed more effectively in the first period than in the second period as shown in Figure 3. The orthophosphate data indicate that the removal was evident during the first two months. However, it has been found that the concentration of orthophosphate in effluents were greater than that in influent on every Monday in this period. This can be attributed to the fact that the final effluent feed solution taken from the sewage treatment plant on every Monday did contain low phosphates; thus the effluents collected on those days may have been mixed with the feed solution of higher phosphate concentration which was fed the day before and was retained overnight in the column as pore liquid. The grab samples collected too soon would have received a large portion of such pore liquid retained mostly near the bottom of the column. Leaching may also be a possible cause of this phenomenon. The low phosphate concentration in the influent fed on each Monday might have functioned as the elution water, since the effect of elution depends on the phosphate concentration gradient between the sand surface and the pore liquid.

Practically no orthophosphates were removed in the second period. The orthophosphate content in the effluents was noted not to be reduced or even increased to a concentration higher than that of influent in most times. This phenomenon which occurred in the second period was not difficult to explain. As has been stated, orthophosphates can be transformed to organic phosphates by metabolic conversion, and the breakdown of bacterial cells will revert organic phosphates to the orthophosphate form; therefore, it becomes clear that an increase in phosphate concentration in the effluent was due to the decay of bacterial mass. In the second period, the bacterial growth may have been sufficiently well developed that some of them may have reached their death phase, so when the dying organisms proceeded their decomposition the orthophosphates were released. As long as the adsorption was approaching saturation so that no great amount of orthophosphates was subsequently adsorbed, the release of orthophosphates by bacterial decomposition would increase the concentration in the effluent.

It has been discovered that no great quantity of condensed phosphates existed in the influent solution of the column. The feed solution was taken from an activated sludge treatment effluent which was found to contain only an average of 1.83 to 2.02 mg/ℓ of condensed phosphates, about 4.2 percent of the total phosphates. This proves that, as mentioned previously, condensed phosphates have a tendency to react with water to undergo hydrolysis to form orthophosphates, especially in an activated sludge treatment plant where they will be hydrolized rapidly. Removal of condensed phosphates ranging from 22.3 percent to 67.3 percent have been observed in this study, indicating that the condensed phosphates in the feed solution still continued their hydrolytic degradation while passing through the sand column.

The organic phosphate data also show the average reduction varied between 23.3 percent and 68.8 percent, although the data do not appear to be very consistent. On the same day, some columns did show a reduction of organic phosphates while other columns might show an increase. However, organic phosphate is the result of biological growth; its concentration represents the organism mass. Thus the reduction of organic phosphate in the effluent may indicate the removal of bacteria cells in the sand layers, while the increased concentration in the effluent may represent the exodus of biological slime from the filter media.

5.2. Phosphate Removal Efficiency Decreased with Time

The rate of total phosphate removal decreased with time, especially in the first period. The removal started at the highest rate in the first week and slowed down. When phosphates in the feed solution were added to the column, they were picked up both by adsorption and assimilation. The adsorption occurs instantly and its effect decreases with time due to saturation of the surface, while the assimilation predominates thereafter when bacterial population builds up to a significant amount. Phosphates will also be adsorbed on biological slimes. As the bacteria grow and multiply, the phosphates adsorbed on the surface of the slime will be assimilated by the bacterial cells and become part of the protoplasm. The quantity of phosphate adsorption will depend on the surface properties of both the sand medium and the bacteria, and the assimilation of phosphates will depend upon the rate of multiplication of the bacteria (50). The phosphate removal rate was less but more constant in the second period than in the first period. This can be explained in that the adsorption effect had almost reached its saturation at the end of the first period, and the bacterial growth had built up and

reached a balanced stage in the second period, so the phosphate removal in this period was mainly due to the biological assimilation.

5.3. Relationship between Feeding Rate and Phosphate Removal

The effectiveness of phosphate removal was found to be a function of feeding rate. The percent removal of total phosphates was in an inverse relation with the dose rate. In other words, the intermittent feed was much more effective in removing phosphates. Taking Columns 1, 2 and 3 for study, one will clearly find that although those three columns were fed with the same amount of sewage per day during the first period, Column 1 receiving a slug loading once a day showed the poorest efficiency, Column 2 fed 4 times a day indicated better removal and Column 3 dosed 12 times a day appeared to be the best one in phosphate removal among the sand columns. This relationship between dose rate and the percent removal held true for both operating periods. However, the removal efficiency also decreased with increasing total flow fed per day. The data of Columns 2, 4 and 5 show this relationship very clearly. Columns 1 and 6 can be taken for further illustration. It was noted that Column 6 improved its removal efficiency relatively in the second period because its dose rate has been reduced 4 times, and the dose rate of Column 1 was increased five times over the original dose so that its removal efficiency reduced relatively. The curves in Figure 25 showing the relationship between dose rate and phosphate removal were plotted without including the data of Column 6 because of its different type of medium. The pea gravel packed in Column 6 was found not so good a filter medium in removing phosphates as the sand medium packed in other columns because of the smaller surface area it presented. The surface is an important factor affecting the phosphate removal.

5.4. Effects of Physical Adsorption and Biological Assimilation

The graphical method used to estimate the quantity of phosphates removed by physical adsorption and biological assimilation separately as shown in Figures 27, 28 and 29 was described in a previous chapter. Actually, the graphs are self-explanatory. The assumption that the phosphate removal in the second period was due to the biological assimilation rather than adsorption is based upon the observation that the phosphate removal during this period was somewhat consistent and much lower as compared to the first period. It is considered that the bacterial growth had been built up and the biological activity had reached its stable level in the second period. The fact that orthophosphate removal decreased extensively while the organic phosphate removal increased relatively in the second period may be used to verify this consideration. The higher removal of orthophosphates in the first period was largely due to the adsorption by the sand medium or slime and when the adsorptive capacity reached its maximum, as in the second period, the removal was limited to that provided by bacterial assimilation. The better removal of organic phosphates is evidently due to the biological uptake of a greater bacterial activity during the second period. However, the date dividing the operating periods does not mean the time when the adsorption mechanism ended; the time separating adsorption and assimilation just happened at the date around the time the operating condition changed by chance. It was not known that the adsorption had reached its saturation when it was decided to rearrange the feeding schedule the tenth week.

The graphical method was only applicable to Columns 2, 3 and 4 because of their unchanged feeding rate throughout the experiment. Among these columns, it is found that Column 2 and Column 3 had similar results in phosphate adsorption, 1850 and 1900 mg of P_2O_5 adsorbed in nineteen weeks

respectively, for both had the same feeding load per day. The difference in the results of biological assimilation, 732 mg in Column 2 and 1178 mg in Column 3, can be attributed to the difference in their dose rates. Again, this reveals that the frequency of dosing is an important factor that should be considered in the practical design of any percolation unit.

5.5. Significance of Column Elution

The results of elution indicate that the phosphates retained in the column, either adhering to the medium surface or sticking in the bacterial slime, can be washed out. The elution was done by adding tap water of about three times the pore volume to the column. The phosphate concentration in the effluent was found very high in the first liter of elution effluent and reduced very rapidly as the elution volume increased. Since the elution curve was made by plotting phosphate concentration in elution, mg/ℓ P_2O_5, against the volume of elution by liters, the area under the curve would equal the amount of phosphates in milligrams elutriated by tap water. By calculating this area, the total amount of phosphates previously adsorbed by the media should be obtained theoretically if the tap water could wash out all the stickings. This was not attempted because the amount so calculated only equals to 2 or 3 percent of the total phosphates removed in nineteen weeks. However, it may take a very large volume of tap water to complete the washing of all the stickings, i.e., to obtain an effluent without any phosphates. In this case the area under the elution curve may extend very far and the missing amount of phosphates may be found in this extended area.

The elution curves of the columns were quite similar to each other except Column 6 which showed the lowest result. This was probably due to the larger pore size in gravel layers and the higher feeding flow applied during

the ordinary operation. As the bacterial slimes grown on the gravel surface became thick enough to be sloughed off, the passing flow would have carried them out to the effluent from time to time.

An investigation on the effect of the elution showed that the phosphate removal rate can be restored to its high initial efficiency by the elutriating treatment. Table 8 shows clearly that the removal efficiency of both Column 4 and Column 5 was greatly increased after elution. This discovery led to the further examination on Column 5. A second elution was applied to this column and the result of second elution did not differ much from that of the first elution. Figure 34 shows the elution curve of Column 5. It seems that the elution curve will be extended as indicated by the dotted line if the intermittent period between elutions is constant, because the elution curve follows a definite pattern. This means that the tertiary treatment in removing phosphates by sand filtration could become practical only if the elution of sand is operated periodically. The elution frequency is dependent on the phosphate removal rate and can be so determined that the elution is performed each time when the percent removal rate drops down to the minimum required efficiency, say 70 percent removal. The operation is just like the backwashing in a rapid filter for water supply, which is dependent upon the head loss. The elution effluent containing high phosphate concentration still remains a waste disposal problem. Yet the volume of this elution waste is much smaller. It seems that this small volume rich in phosphate could be discharged to a storage lagoon to cultivate algae for cattle feed; or to a sand drying bed to evaporate the water content; or possibly to a farm field for agricultural irrigation and fertilization.

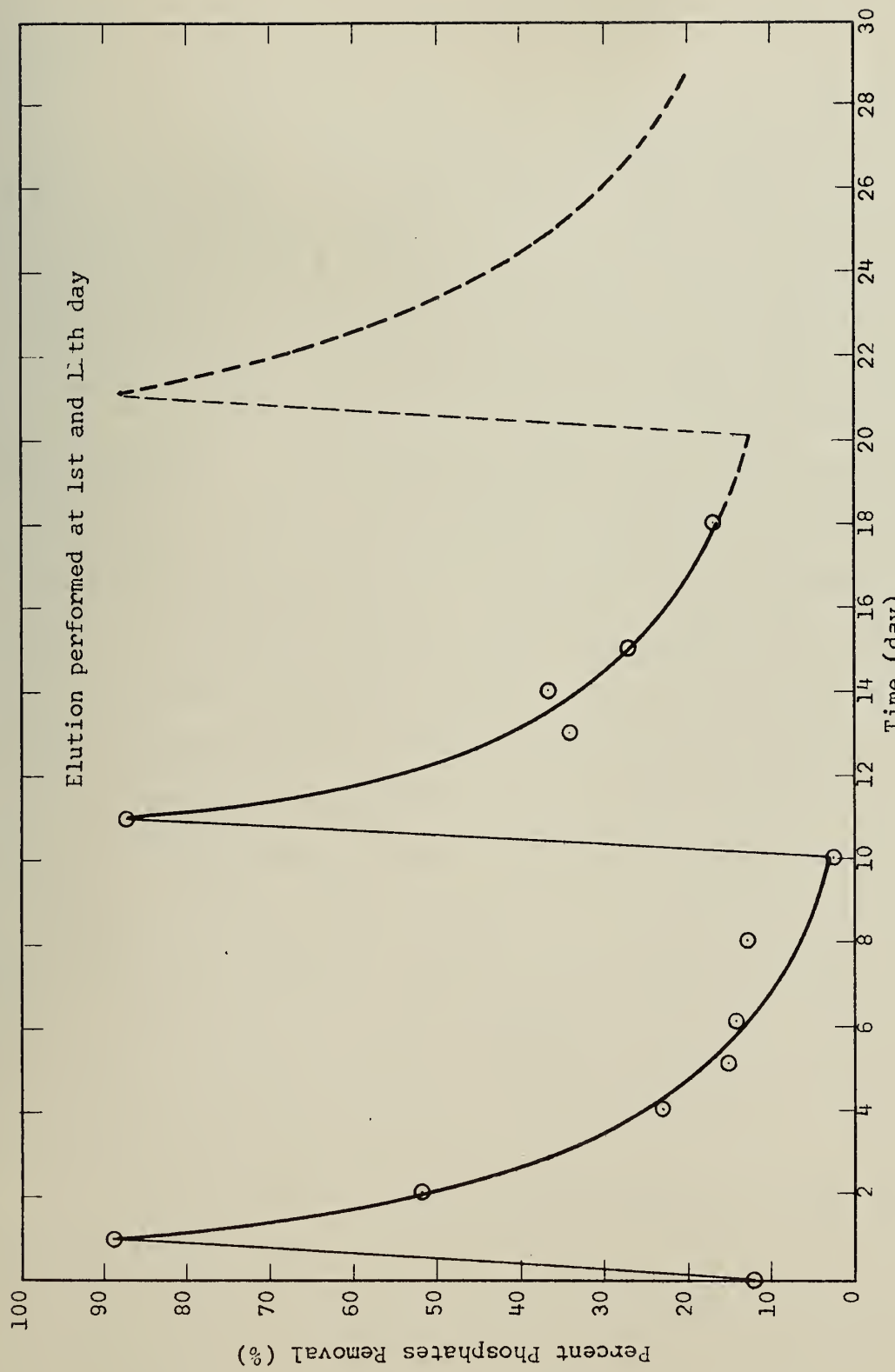


Figure 34. Elution Curve of Column 5

CHAPTER 6: CONCLUSIONS

The following conclusions are drawn from the discussions and results presented in the preceding chapters.

1. The average percent removal of total phosphates was much higher in the first period than in the second period. Orthophosphate removal was evident in the first period, ranging from 11.6 percent to 31.3 percent, but no significant amount was removed in the second period. The feed solution taken from an activated sludge treatment effluent did not contain much condensed phosphates. Only about 4.2 percent of the total phosphates was in the form of condensed phosphates. In both operating periods, the condensed phosphates were reduced by 22.3 percent to 67.8 percent after passing through the columns. The reduction rate of the organic phosphates ranged from 23.3 percent to 68.8 percent. The reduction in every column in the second period was greater than that in the first period except Column 2 which was fed in the second period with a synthetic solution containing higher organic phosphate source.

2. Adsorption and assimilation are two major mechanisms in removing phosphates in the sand columns. In the first period, phosphate removal was mainly accomplished by the physical adsorption on the column media, so the phosphate removal rate decreased with time as the adsorptive capacity approached its limit. In the second period, the biological assimilation predominated, phosphate removal was mostly done by the bacterial activities, so the removal rate did not vary much during the period.

3. The effectiveness of the phosphate removal is a function of feeding rate. Although high total flow fed per day did reduce the efficiency of the column, the major factor affecting phosphate removal was the dose rate or the dosing frequency. The percent removal of total phosphates was inversely proportional to the hydraulic loading per dose. The intermittent feed was

much more effective in removing phosphates. The best result was obtained by dosing the sand column 12 times a day at a dose rate of 10.3 - 11.6 lbs P_2O_5/acre/dose.

4. Coarse gravel was not a good filter medium in removing phosphates as compared to the sand. Column 6 packed with pea gravel showed the poorest efficiency at all times.

5. The amount of total phosphates removed by adsorption and assimilation separately was estimated by a graphical method applied to the columns with an unchanged feed. The result indicates that an average of 34.7 percent of the total removal was due to the biological uptake and the rest, 65.3 percent, was due to the physical adsorption. The quantity of P_2O_5 removed by each column ranged from 2585 mg to 7852 mg.

6. The phosphates retained in the column can be washed out. A few percent of the phosphates accumulated in the column during nineteen weeks can be elutriated off by about three pore volumes of tap water. From 22.5 to 95.5 mg of P_2O_5 was recovered in each elution.

7. The phosphate removal efficiency of the column increased tremendously after being elutriated with tap water. The efficiency then decreased with time as previously, but a second elution will restore its effectiveness again. Thus, it seems that the method of elution provides a possibility to maintain a high efficiency in removing phosphates if the elution process can be performed periodically. It can be predicted that an effective tertiary treatment in removing phosphates from the secondary treatment effluent by sand filtration can only be accomplished if the unit is intermittently fed and periodically elutriated. However, the elution waste provides a further disposal problem. A storage lagoon or a drying bed might be required to solve this problem. The elution waste containing high phosphates is also a good fertilizer for agricultural irrigation.

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APPENDICES

Appendix A

Procedures for the Determination of Ortho-, Condensed, and Total-Phosphates

I. Orthophosphate

1. Transfer an appropriate volume of sample into a 100 ml extraction cylinder. Dilute to 40 ml with distilled water. (Also run a blank containing 40 ml distilled water.)

2. Add exactly 50 ml of Benzene-isobutanol mixture.

3. Add 15 ml of acidic molybdate reagent.

4. Shake vigorously without delay for exactly 15 seconds.

5. Remove the stopper, as soon as the layer has separated, withdraw a 25 ml of supernatant. Transfer to a 50 ml flask.

6. Add about 15 ml alcoholic sulfuric acid and swirl.

7. Add 1 ml diluted freshly prepared stannour chloride solution, swirl and make to the mark with alcoholic sulfuric acid.

8. Mix well and allow to stand 10 minutes before measuring percent transmission on a Coleman spectrophotometer at a wave length of 630 mμ (use red filter).

II. Total Inorganic Phosphate

1. Add 8 ml of 8/N H_2SO_4 to an appropriate sample and dilute to 48 ml in a 100 ml flask.

2. Insert the flask into water-bath, boil gently for 40 minutes.

3. After cooling, transfer into a 100 ml extraction cylinder. (Make up to 48 ml with distilled water if less than 48 ml.)

4. Add 50 ml of Benzene-isobutanol mixture and 8 ml of 10 percent ammonium molybdate.

5. Shake vigorously for at least 15 seconds.

6. Complete the procedure as described in Step 5 of Procedure I.

Condensed phosphate = Total inorganic phosphate - Orthophosphate

= Procedure II - Procedure I

III. Total Phosphates (including organic phosphates)

1. Place an appropriate sample in 500 ml Erlenmeyer flask of the wet-ashing apparatus. Dilute to 40 ml with distilled water.

2. Add 10 ml of concentrated nitric acid.

3. Add 6 ml conc. sulfuric acid and boil down to fumes of SO_3.

4. Place the tube from the flask containing 300 ml of 10 percent sodium hydroxide in the neck of the sample flask and turn on the water aspirator.

5. Two more 10-ml additions of HNO_3 must be made and removed by fuming to insure complete decomposition of the organic phosphates.

6. Continue boiling until all the nitric acid is driven off.

7. Cool to room temperature and carefully add 60 ml distilled water. Boil for 25 minutes. Transfer to a 500 ml extraction cylinder. (Rinse the flask.)

8. Dilute the sample to 225 ml. Add 17 ml of isobutanol.

9. Add exactly 50 ml of benzene-isobutanol.

10. Add 25 ml of neutral molybdate reagent. Stopper the cylinder and shake vigorously for 1 minute.

11. Complete the procedure as described in Step 5 of Procedure I.

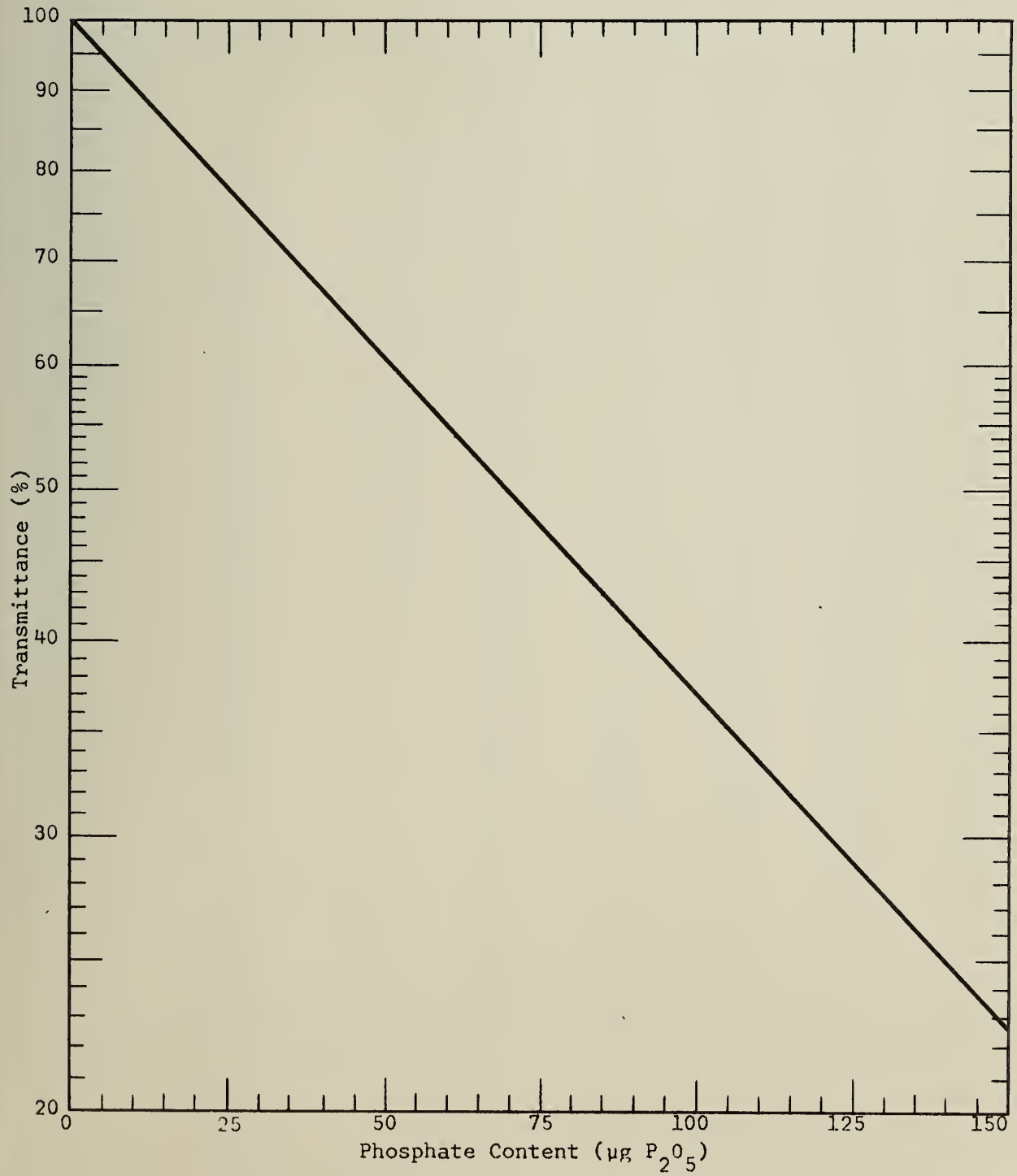
Organic phosphates = Total phosphates - Inorganic phosphates

= Procedure III - Procedure II

Appendix B

Calibration Curve for the Determination of Phosphate Concentration

The calibration curve was made by using a Coleman Spectrophotometer at wave length 630 mμ with a red filter.



Appendix C

Data of Phosphate Concentration in Column Influents and Effluents

The following data are obtained from the experiment by using the analytical methods described in Appendix A. All phosphate concentrations are in terms of mg/ℓ P_2O_5.

Table 11

ORTHOPHOSPHATE CONCENTRATION IN COLUMN INFLUENTS AND EFFLUENTS (FIRST PERIOD)

Date	Influent	Effluents					
		(1)	(2)	(3)	(4)	(5)	(6)
7/3/63	28.0	8.3	4.0	3.0	8.5	16.0	24.0
7/4/63	36.6	23.0	15.0	10.0	17.0	23.0	33.0
7/8/63*	15.7	14.4	14.5	14.6	25.5	13.7	14.0
7/9/63	26.0	18.7	12.5	12.0	14.5	15.1	17.3
7/10/63	23.5	16.0	18.2	17.2	22.5	24.0	22.0
7/12/63	31.2	22.3	24.2	25.0	20.8	20.0	29.5
7/15/63*	18.9	23.0	29.2	28.3	27.2	28.3	25.3
7/16/63	32.0	20.0	23.9	17.9	18.0	19.5	28.3
7/19/63	27.0	23.8	25.8	22.5	26.2	27.2	27.4
7/22/63*	14.4	18.1	19.4	21.5	18.1	16.5	13.5
7/23/63	36.2	21.2	16.9	18.3	23.0	16.9	33.8
7/24/63	24.2	21.5	20.7	14.4	18.0	17.8	26.5
7/25/63	32.3	25.0	24.9	23.5	24.2	23.0	31.7
7/26/63	66.7	33.0	25.3	26.5	30.7	31.1	39.0
7/29/63*	14.8	36.8	50.0	42.5	48.5	53.3	66.0
7/30/63	52.0	30.0	35.2	27.4	36.5	23.2	39.5
7/31/63	40.0	35.0	39.2	38.7	38.0	43.5	41.3
8/1/63	23.5	34.6	39.0	43.6	38.9	40.0	28.6
8/2/63	29.0	24.3	28.0	26.1	25.7	23.0	26.7
8/5/63*	15.8	22.0	25.2	26.2	28.0	26.5	26.6
8/6/63	46.7	25.3	25.2	25.0	29.1	34.0	34.5
8/7/63	46.9	23.8	26.0	26.0	29.3	32.2	32.3
8/8/63	22.9	34.5	45.6	47.0	51.5	53.5	27.2
8/9/63	34.2	33.1	32.2	33.1	30.0	28.7	30.0
8/12/63*	36.0	22.9	22.7	23.2	22.4	20.0	25.0
8/13/63	55.0	28.0	30.0	30.4	33.7	32.8	50.0
8/14/63	33.0	39.2	50.7	49.7	51.5	49.2	44.4
8/15/63	38.1	32.1	30.0	30.4	31.2	34.0	41.5
8/19/63	55.5	39.2	43.7	43.7	45.0	43.7	51.6
8/21/63	37.0	32.8	32.7	33.2	31.3	29.3	28.7
8/22/63	45.0	36.5	35.4	32.3	34.3	33.2	42.6
8/23/63	41.8	39.2	39.0	41.1	34.0	35.3	37.9
8/26/63*	53.5	50.7	38.3	36.8	39.0	33.0	47.5
8/27/63	49.2	45.8	45.0	49.2	44.0	50.6	50.4
8/28/63	50.4	43.0	47.8	49.0	46.1	50.5	52.0
8/30/63	42.0	40.0	39.5	38.2	39.2	41.1	41.0

*Monday

Table 12

ORTHOPHOSPHATE CONCENTRATION IN COLUMN INFLUENTS AND EFFLUENTS (SECOND PERIOD)

Date	Influents*		Effluents					
	A	B	(1)	(2)	(3)	(4)	(5)	(6)
9/20/63	48.2	27.3	47.9	28.7	46.1	46.3	42.0	48.4
9/23/63	53.0	27.0	53.2	29.5	50.5	51.0	53.0	52.8
9/25/63	47.2	27.5	64.0	31.2	51.8	46.3	48.1	49.2
9/28/63	47.0	26.1	51.3	36.3	46.3	46.8	46.2	49.1
10/1/63	63.0	30.5	60.0	30.6	49.6	49.1	59.5	62.5
10/2/63	55.0	31.4	55.0	29.5	47.8	47.1	56.0	62.6
10/3/63	50.1	27.6	50.0	26.7	49.5	50.0	50.1	46.2
10/4/63	57.6	24.0	57.8	27.3	50.6	51.0	58.0	56.8
10/5/63	43.0	25.8	23.0	47.1	42.4	42.8	44.0	41.0
10/8/63	34.6	23.6	35.0	21.8	37.0	36.9	35.2	36.6
10/10/63	38.6	22.0	39.0	27.8	33.6	38.9	35.0	36.0
10/12/63	37.0	23.0	34.1	27.0	40.9	38.0	37.5	37.0
10/15/63	44.0	40.9	48.1	37.0	42.5	39.2	40.1	43.8
10/17/63	47.4	37.0	47.0	34.9	47.1	46.2	54.0	44.7
10/22/63	36.4	39.2	34.0	47.6	34.1	38.2	34.7	41.2
10/24/63	47.7	37.0	46.4	34.5	40.8	43.3	53.0	47.2
10/26/63	46.0	32.7	52.1	32.5	45.0	44.5	48.9	45.8
10/28/63	49.0	50.6	53.0	49.1	52.1	52.1	55.7	57.0
10/31/63	35.0	53.2	35.4	50.0	34.2	34.7	36.0	37.0
11/2/63	47.8	49.4	44.0	47.6	48.7	47.7	48.0	48.2
11/5/63	46.8	49.1	44.9	55.6	47.7	42.7	47.6	47.0
11/7/63	49.0	53.0	49.3	50.7	50.2	51.1	49.8	49.1

*Influent A -- Sewage of secondary treatment effluent.

Influent B -- Synthetic feeding solution. (For Column 2 only.)

Table 13

CONDENSED PHOSPHATE CONCENTRATION IN COLUMN INFLUENTS AND EFFLUENTS (FIRST PERIOD)

Date	Influent	Effluents					
		(1)	(2)	(3)	(4)	(5)	(6)
7/3/63	0.9	0.7	0.2	0.9	0.4	0.3	0.5
7/4/63	0.8	0	0.3	0	0	0.2	0.7
7/9/63	3.2	1.6	0	2.0	1.6	2.5	3.2
7/12/63	0.6	0	0.2	0	0.5	0	0
7/16/63	1.4	1.3	0	0.1	1.1	0	1.3
7/19/63	3.1	3.1	0.1	1.5	1.1	3.0	2.9
7/23/63	2.3	1.6	1.9	1.5	2.0	2.2	2.4
7/25/63	0.7	0.3	0	0.1	0.6	0	0.1
7/30/63	1.4	1.8	0.7	0	0	0	0.6
8/2/63	1.1	0.5	0	0	0.5	0.6	0.3
8/6/63	0.8	0.6	0.1	0	0	0.2	0
8/9/63	1.8	0	0.7	0	0.5	0	0.8
8/12/63	3.0	1.6	1.4	1.0	1.7	2.5	3.2
8/13/63	2.7	0.8	2.2	1.8	3.0	0	2.6
8/19/63	2.2	0	0	2.4	0.9	2.6	2.1
8/22/63	1.9	1.6	0.4	0	0.3	1.5	1.1
8/23/63	1.8	1.2	1.0	0	0.2	1.7	2.4
8/26/63	2.3	2.8	1.7	0.5	3.5	0.7	0.5
8/27/63	2.8	2.4	2.4	0	0	1.1	1.6
8/30/63	1.7	0	0	0	1.3	1.5	2.0

Table 14

CONDENSED PHOSPHATE CONCENTRATION IN COLUMN INFLUENTS AND EFFLUENTS (SECOND PERIOD)

Date	Influents*		Effluents					
	A	B	(1)	(2)	(3)	(4)	(5)	(6)
9/20/63	0.8	2.0	1.2	0.2	1.1	0.9	0.2	0
9/23/63	1.6	2.1	0.8	0	0	1.4	0	1.1
9/28/63	1.5	0.4	0.9	0.8	0	0	1.3	1.5
10/3/63	2.5	3.0	0	1.4	2.6	2.4	1.8	0
10/5/63	5.0	1.0	4.5	0	2.0	3.7	3.9	2.1
10/10/63	0	0	2.4	0.7	1.2	0	2.1	0
10/12/63	2.2	2.4	1.6	0.2	0.8	0.2	0.4	0.9
10/15/63	2.4	0.9	0	0	0	0.1	0	0.1
10/17/63	1.0	0	0	0	0.8	0	0.7	0
10/22/63	0	0.8	1.2	1.2	1.1	2.0	1.0	0.2
10/24/63	2.8	1.7	1.5	0.2	0.1	0.4	0.9	3.0
10/26/63	5.6	1.8	0	1.2	0	1.2	0	0
10/28/63	2.9	2.0	1.8	1.8	1.2	0	0.2	0.7
10/31/63	0	2.3	0.2	0	1.0	1.2	1.2	0.8
11/5/63	1.7	0.2	0.7	0.9	0	1.9	0	0
11/7/63	2.3	0.4	1.8	1.1	2.5	0	2.0	1.1

*Influent A -- Sewage of secondary treatment effluent.

Influent B -- Synthetic feeding solution. (For Column 2 only.)

Table 15

ORGANIC PHOSPHATE CONCENTRATION IN COLUMN INFLUENTS AND EFFLUENTS (FIRST PERIOD)

Date	Influent	Effluents					
		(1)	(2)	(3)	(4)	(5)	(6)
7/3/63	0	0.2	1.8	4.4	0	0	0
7/4/63	3.8	0.4	1.2	1.6	0.4	2.5	6.0
7/9/63	0	1.0	0.7	0	0	0	0
7/12/63	3.4	0	0.3	0	0	0.2	0.6
7/16/63	2.2	0.7	0	0.5	8.7	6.3	0
7/19/63	0.3	0.6	0.2	0.2	0	0	0
7/23/63	1.4	2.2	0	1.2	1.0	2.0	2.4
7/25/63	3.0	0.2	0.6	0.1	0.2	2.3	0
7/30/63	3.5	0	1.0	1.4	1.0	1.7	0.4
8/2/63	1.5	0.7	0.7	1.5	0.6	1.5	3.0
8/6/63	0.8	0	1.7	0	0.8	0	0
8/9/63	1.2	0.2	0	0.2	0.8	2.1	0
8/12/63	0.6	0	0	0.3	0.6	0	1.8
8/13/63	1.3	0.9	1.1	1.1	0.6	0.8	1.0
8/19/63	5.3	1.1	0.8	0.6	0.9	4.3	0.9
8/22/63	1.2	1.5	0	0.6	0.6	0.3	1.1
8/23/63	2.4	0.1	0.6	0.3	1.3	0.8	0.9
8/26/63	4.2	1.6	1.1	1.9	1.7	3.1	3.6
8/27/63	4.5	2.8	0.7	0.3	0.8	0.8	1.6
8/30/63	3.5	1.3	2.3	2.5	2.2	3.5	3.7

Table 16

ORGANIC PHOSPHATE CONCENTRATION IN COLUMN INFLUENTS AND EFFLUENTS (SECOND PERIOD)

Date	Influents*		Effluents					
	A	B	(1)	(2)	(3)	(4)	(5)	(6)
9/20/63	0.2	6.0	0.2	4.0	0.1	0	0	1.1
9/23/63	3.4	4.8	0	3.1	0	0	3.0	2.8
9/28/63	2.7	4.2	0	2.7	0.2	0	0	1.5
10/3/63	3.1	5.1	1.7	4.1	0.9	3.2	2.8	1.6
10/5/63	6.0	7.0	4.2	3.8	5.1	3.8	2.9	4.5
10/10/63	0	1.0	0	0.9	0.2	0.1	0.3	0.1
10/12/63	0.8	3.0	0	0	2.1	1.2	0.3	0
10/15/63	2.1	0	0	0.1	0	0	2.0	1.3
10/17/63	2.6	4.0	2.0	2.0	0	2.4	3.0	0
10/22/63	3.5	0	1.2	0	1.2	0	1.8	0
10/24/63	0	7.0	0	2.8	0.8	1.2	1.6	1.2
10/26/63	0	2.6	0	3.7	1.7	0	0.8	0.6
10/28/63	2.7	5.8	1.1	3.4	0	0.1	0.4	2.4
10/31/63	1.2	4.9	0	6.0	1.3	1.1	0.2	0.4
11/5/63	3.1	1.2	0	0.8	0	1.7	0	0
11/7/63	1.8	6.2	0	3.2	1.2	0	0	0

*Influent A -- Sewage of secondary treatment effluent.

Influent B -- Synthetic feeding solution. (For Column 2 only.)

Table 17

TOTAL PHOSPHATE CONCENTRATION IN COLUMN INFLUENTS AND EFFLUENTS (FIRST PERIOD)

Date	Influent	Effluents					
		(1)	(2)	(3)	(4)	(5)	(6)
7/3/63	28.9	9.2	6.0	8.3	8.9	16.3	24.5
7/4/63	41.2	27.2	16.5	11.6	17.4	25.7	39.7
7/9/63	29.2	21.3	13.2	14.0	16.1	17.6	20.5
7/12/63	35.]	22.3	24.7	25.0	21.3	20.2	30.1
7/16/63	35.6	22.0	23.9	18.5	27.8	25.8	29.6
7/19/63	30.4	27.5	26.1	24.2	27.3	30.2	30.3
7/23/63	39.9	25.0	28.8	21.0	26.0	21.1	38.6
7/25/63	36.0	25.5	25.5	23.7	25.0	25.3	31.8
7/30/63	56.9	31.8	36.9	28.8	31.5	23.9	40.5
8/2/63	31.6	25.5	28.7	27.6	26.8	25.1	30.0
8/6/63	48.3	25.9	27.0	25.0	29.9	34.2	34.5
8/9/63	37.2	33.3	32.9	33.3	31.3	30.8	30.8
8/12/63	39.6	24.5	24.1	24.5	24.7	22.5	30.0
8/13/63	59.0	29.7	33.3	33.3	37.3	33.6	53.6
8/19/63	63.0	40.3	44.5	46.7	46.8	50.6	54.6
8/22/63	48.1	39.6	35.8	32.9	35.2	35.0	44.8
8/23/63	46.0	40.5	40.6	41.4	35.5	37.8	41.2
8/26/63	60.0	55.1	41.1	39.2	44.2	36.8	51.6
8/27/63	56.5	51.0	48.1	49.5	44.8	52.5	53.6
8/30/63	47.2	41.3	41.8	40.7	42.7	46.1	46.7

Table 18

TOTAL PHOSPHATE CONCENTRATION IN COLUMN INFLUENTS AND EFFLUENTS (SECOND PERIOD)

Date	Influents*		Effluents					
	A	B	(1)	(2)	(3)	(4)	(5)	(6)
9/20/63	49.2	35.5	49.3	32.9	47.3	47.2	42.2	49.5
9/23/63	58.0	33.9	54.0	32.6	50.5	52.4	56.0	56.7
9/28/63	51.2	30.7	52.2	39.8	46.5	46.8	47.5	52.1
10/3/63	55.7	35.7	51.7	32.2	53.5	55.6	54.7	47.8
10/5/63	54.0	33.8	55.8	26.8	49.5	50.3	50.8	47.6
10/10/63	38.6	23.0	41.4	29.7	35.0	39.0	37.4	36.1
10/12/63	40.0	28.4	35.7	27.2	43.8	39.4	38.2	37.9
10/15/63	48.5	41.8	48.1	37.1	42.5	39.3	42.1	45.2
10/17/63	51.0	41.0	49.0	36.9	47.9	48.6	57.7	44.7
10/22/63	39.9	40.0	36.4	48.8	36.4	40.2	37.5	41.4
10/24/63	50.5	45.7	48.9	37.5	41.7	44.9	55.5	51.4
10/26/63	51.6	37.1	52.1	37.4	46.7	45.7	49.7	46.4
10/28/63	54.6	58.4	55.9	55.3	53.5	52.2	56.3	60.1
10/31/63	36.2	60.4	35.6	56.0	46.5	37.0	37.4	38.2
11/5/63	51.6	50.5	45.6	57.3	47.7	46.3	47.6	47.0
11/7/63	53.1	59.6	51.1	55.0	53.8	51.1	51.8	50.2

*Influent A -- Sewage of secondary treatment effluent.

Influent B -- Synthetic feeding solution. (For Column 2 only.)

Table 19

PERCENTAGE REMOVAL OF TOTAL PHOSPHATES (FIRST PERIOD)

Date	Column No.					
	(1)	(2)	(3)	(4)	(5)	(6)
7/3/63	68.2	79.2	71.3	69.2	43.6	15.2
7/4/63	34.0	59.9	71.8	57.6	37.6	3.7
7/9/63	27.0	54.7	52.0	44.8	39.6	29.7
7/12/63	36.7	29.8	28.9	39.5	42.6	14.5
7/16/63	38.2	32.8	48.0	21.8	27.5	16.8
7/19/63	9.5	14.1	20.3	10.2	0.7	0.3
7/23/63	37.4	27.8	47.4	34.8	47.1	3.2
7/25/63	29.3	29.3	34.2	30.7	39.8	11.5
7/30/63	44.2	35.2	49.4	43.6	58.1	28.8
8/2/63	19.3	9.2	12.7	15.3	20.7	5.2
8/6/63	46.4	44.1	48.3	38.2	29.2	28.6
8/9/63	10.4	11.5	10.4	15.8	17.2	17.2
8/12/63	38.2	39.2	38.2	37.7	43.2	24.3
8/13/63	50.3	43.6	43.6	36.8	43.1	9.2
8/19/63	36.2	29.5	26.0	25.8	19.8	13.4
8/22/63	17.7	25.6	31.7	26.8	27.3	7.0
8/23/63	12.2	11.8	10.1	23.0	17.9	10.6
8/26/63	8.2	31.6	34.9	26.3	38.8	14.2
8/27/63	9.6	14.7	12.2	20.6	6.9	5.0
8/30/63	12.5	11.4	13.7	9.5	2.3	1.1
Average	29.28%	31.75%	35.26%	31.40%	30.15%	12.98%

Table 20

PERCENTAGE REMOVAL OF TOTAL PHOSPHATES (SECOND PERIOD)

Date	Column No.					
	(1)	(2)	(3)	(4)	(5)	(6)
9/20/63	0	6.7	3.8	4.1	14.2	0
9/23/63	6.8	3.8	12.8	9.6	3.4	2.2
9/28/63	0	0	9.1	8.6	7.2	0
10/3/63	7.2	9.8	3.8	0.2	1.8	13.9
10/5/63	0	0.7	8.3	6.8	5.8	11.8
10/10/63	0	0	9.3	0	3.1	6.4
10/12/63	10.7	4.2	0	1.5	4.5	5.2
10/15/63	0.8	9.5	12.3	19.0	13.2	6.8
10/17/63	3.9	10.0	6.1	4.7	0	12.3
10/22/63	8.7	0	8.7	0	6.0	0
10/24/63	3.2	17.9	17.4	11.1	0	0
10/26/63	0	0	9.5	11.4	3.7	10.1
10/28/63	0	5.2	2.3	4.4	0	0
10/31/63	1.7	7.3	0	0	0	0
11/5/63	11.7	0	7.7	10.2	7.7	8.8
11/7/63	3.7	7.7	0	3.7	2.5	5.4
Average	3.65%	6.42%	6.95%	5.83%	4.51%	5.18%

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